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REPORT OF PETROLEUM AND NATURAL-GAS DIVISION

FISCAL YEAR 1947

BY

R. A. CATTELL AND OTHERS

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UNITED STATES DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

REPORT OF PETROLEUM AND NATURAL-GAS DIVISION, FISCAL YEAR 1947[1]

By R. A. Catlell[2] and others

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SUMMARY

Since the return of the Petroleum and Natural Gas Division of the Bureau of Mines to normal peacetime functions following World War II, a coordinated program of oil and gas development and production research has been in progress, and the importance of the problems has been evaluated so that the Bureau can render greater service to the oil and gas industry.

Among the problems associated with development and production research, those concerned with efficient utilization of the Nation's reserves of hydrocarbons contained in gas-condensate type reservoirs continue to receive major emphasis. For a number of years an important part of the Bureau's work has been the study of two pressing problems associated with production from such reservoirs; first, an investigation of fluid properties, and the second, finding a means of controlling corrosion. Studies of the characteristics of gas-condensate fluids have resulted in the publication of a number of reports, which cover a broad field. In general they deal with subjects such as the properties of a fluid from a well, development of research equipment, means of combatting corrosion, and the many aspects of gas-condensate engineering. To provide experimental data on relative liquid and gas volumes and critical pressures and temperatures, a windowed cell was constructed that permits observation of the fluid phase while making the tests.

Experimentation in the field on the use of inhibitors to control corrosion of equipment in gas-condensate wells has disclosed that solutions of chromate are effective retardants of corrosion.

Engineering field studies of the Carthage and New Hope gas-condensate fields are in progress, and reports on the Sheridan and Lake Creek fields have been completed.

Following a plan of making studies of important newly discovered oil fields, the Bureau is investigating the physical properties of reservoir oil

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from the North Lindsay, Okla., field, and a preliminary report of the field will be furnished the industry.

At the request of the United States Navy, the Bureau of Mines, during the war period, made a study of reservoir oils from five wells in the shallow zones of the Naval Petroleum Reserve No. 1, Elk Hills field, Calif. The results of this study have now been published and include (1) pressure-volume-temperature and viscosity data, (2) correlation of some physical properties with A.P.I. gravities of produced oils, and (3) the application of material-balance concepts to a newly discovered oil reservoir that resulted in increasing the proved oil reserve.

The Bureau's studies of the optimum spacing of oil wells now in progress for several years were continued, with emphasis on theoretical and field investigations of various aspects of the problem. The goal is to find practical means for determining the minimum number of wells that should be drilled in oil fields to effect maximum oil recovery consistent with profitable operation.

In cooperation with the American Petroleum Institute and several oil companies, the Bureau is carrying out a series of tests to find improved methods for measuring the degree of contamination of cores by drilling-fluid filtrates.

Increased interest in secondary recovery methods of oil production has resulted in numerous requests from the general public, trade associations, and trade journals for results of the Bureau of Mines secondary-recovery studies and for information about the work.

As a result of this expanding interest, Bureau engineers have worked closely with several agencies interested in this vitally important problem, including the Interstate Oil Compact Commission, American Petroleum Institute, Pennsylvania Grade Crude Oil Association, the North Texas Oil and Gas Association, and others. Field studies of waterflooding projects are in progress, and the results obtained in 11 typical waterflooding projects in north and north-central Texas have been published.

Experimentation was continued on the engineering fundamentals involved in flowing instead of pumping oil wells on air-gas injection secondary-recovery projects in the Appalachian area. To date, all of the fundamental relationships proved in the laboratory have been applied successfully to field practice.

An engineering, statistical analysis of the results of clean-out operations in southern Pennsylvania, West Virginia, and southeastern Ohio was published during the fiscal year 1947. This report on reconditioning methods and results in use in the southern Appalachian fields is particularly timely, as there are many wells in that area in dire need of remedial work.

In connection with the secondary recovery work, a study was initiated of methods and materials that might be used to plug selectively the most permeable parts of oil-sand reservoirs after the recoverable oil has been removed

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for the purpose of preventing these formations from taking fluid in the input wells in water-flooding and gas-repressuring operations.

The development of a process for recovering oil from bituminous-sandstone deposits near Edna, in San Luis Obispo County, Calif., has continued to receive consideration. Significant increases in efficiency and economics of operation of the laboratory separation plant were achieved by (1) reduction in power cost, (2) elimination of expensive reagents previously used as dewatering and desilting aids, and (3) the elimination of one of the pulping agents with an appreciable reduction in cost if the separated bitumen is to be cracked by the thermal process for distillates and coke.

A study of gravity drainage oil through sand by means of a miniature oil-field model was completed during the year. The results of core analyses showed that the residual oil saturations were low at the top of the sand and increased gradually with depth. Experiments in heating the oil sand had been conducted, and the results of the temperature study showed that the increase in mean temperature throughout the sand body was insufficient to reduce the viscosity of the oil enough to increase drainage of the oil through the sand.

The current broad objectives of research in petroleum chemistry and refining is to obtain a complete picture of the availability of fuels for all types of internal-combustion engines. The problem includes raw-material studies, relationships of fuel composition, properties and performance, utilization of petroleum products, and analytical methods.

Additional data were obtained on low-temperature calorimetry, combustion calorimetry, and statistical calculations as part of the project to obtain precise and accurate values of the fundamental thermodynamic properties of the hydrocarbons found in petroleum and those for the related compounds that can be derived from petroleum by means of chemical reactions. Accurate knowledge of these properties of the pure compounds will enhance the value of petroleum as a source material for needed products.

Natural-gas research includes a cooperative study with the Natural Gas Department of the American Gas Association of the factors influencing flow of gas in pipe lines and studies of ways and means for removing nitrogen from natural gas.

Helium activities continue to be an important part of the Bureau's research, which is directed toward appraisal of the Nation's helium resources, improvements in processing cycles and equipment, and increasing its utilization through development of new uses and better procedures.

INTRODUCTION

The Petroleum and Natural Gas Division of the Bureau of Mines was just completing formulation of its post-war plans for research on oil and gas problems as the fiscal year 1946 closed. Now, a year later, the Division can appraise its plans in the light of a year's work without the disruption of actual warfare, take account of the developing needs of the industry, and

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modify its program where necessary. When these plans were first formulated efforts were being made to turn from war assignments to the main normal functions of the Division under peacetime conditions. Readjustments in personnel assignments were necessary as veteran employees returned to their earlier civilian duties or decided to follow other lines of activity. Furthermore, many difficulties were met in finding available, qualified technical employees to fill the gaps or to take on new assignments. On the whole, however, the main administrative problems were the result of the need to determine the place of the Bureau of Mines in oil and gas research under the peacetime national economy as modified by the late war.

To that end, the technologists of the Division discussed among themselves and with industry representatives such subjects as: What types of problems does the industry believe the Bureau should study? What are the specific problems requiring first attention? What are the types of problems the Bureau is best qualified to undertake? As a result of these discussions and conferences, a program was developed to encompass those problems the solutions of which are needed urgently by industry and Government.

Another aspect of the return to normal functions is the careful consideration that has been and is being given to the dissemination of information so that it will do the most good after it has been collected. A timely opportunity along this line was an invitation from the Division of Chemical Education of the American Chemical Society, in collaboration with the Division of Petroleum Chemistry, of the same organization, to participate in a symposium on petroleum information surveys at the meeting of the American Chemical Society at Atlantic City in April 1947. The Bureau contributed a paper describing its methods of disseminating information,3/ and a selected list of Bureau publications in the field of chemistry and refining was distributed at this meeting. Other selected lists dealing with primary production of oil, secondary recovery, natural gas, thermodynamics, and a wide variety of allied subjects, including helium and oil shale, are being brought to date and made publicly available as reference material.

How to help develop and conserve the Nation's resources and to find methods by which nature may be made to pay larger dividends from its still undeveloped resources in oil and gas has been a prompting thought in all of the deliberations. Planning with the long view presupposes that industry, Government, and individuals are willing to make the necessary capital investment of time, energy, and money. In other words, aside from the ever-present need for considering problems of national security, the Bureau's philosophy in the conduct of all of its work on petroleum and natural gas is to develop facts that may be applied so that true conservation may result. As Joseph A. Holmes, first director of the Bureau of Mines, pointed out years ago, true conservation rules out the implications of hoarding and urges the practice of "a wiser and more efficient use of our natural resources."

3/ Smith, H. M., Gooding, R. M., Ball, J. S., The Role of the Bureau of Mines in Dissemination of Information Relating to Petroleum Chemistry and Refining: Presented at the meeting of the American Chemical Society, Division of Petroleum Chemistry, Atlantic City, April 1947.

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The Bureau of Mines extracts large quantities of helium from natural gas. Helium is a natural resource and available in large quantities only in the United States. This gas continues to win acceptance by American industry while retaining its specialized values to the military forces, and it is only natural that both industry and Governmental agencies look to this Bureau for new developments and improvements in extraction techniques and uses of helium. A well-balanced research program is providing progress by developing and installing equipment for the production of higher-purity helium required for some new uses; developing new and better techniques in the use of helium in welding and metallurgy; developing more efficient helium extraction through a study of higher-pressure separation of helium and a study of the removal of nitrogen from natural gas; locating and acquiring new helium reserves; studying processes and developing equipment for cheaper means of transporting helium; improving continually the quality of helium shipped; and finding new uses for helium, such as its use in tracing the flow of oil and gas underground and finding leaks in casings of oil and gas wells.

The medical use of helium continues to increase, and helium is taking an increasingly important place in the national economy through use on a nationwide scale in the fabrication of new and modern products. Certain metals and alloys have been fabricated through the use of the helium shielded-arc welding process where such fabrication has been impossible without the use of helium. Helium shielded-arc welding is being applied to the welding of metals such as aluminum, stainless steel, magnesium, copper, and inconel, and as of this date it is the only known process for welding titanium, a metal offering much promise as a new material for construction.

As evidence of the increasing importance of helium to the Nation, the commercial sales of helium for the fiscal year 1947 were about nine times greater than in any pre-war year and over three times any previous year. The total sales were approximately twice the previous year and over three times any pre-war year. The sale of helium to commercial concerns not only enables the Nation to produce products not enjoyed by other countries but also provides adequate facilities to produce helium for the Government for both peacetime and wartime use. Helium being produced at present from natural gas is the means of conserving a commodity that would otherwise go to fuel market in the natural gas and be lost. The immediate availability of helium during the last war was proof of the wisdom of a strong Government organization for the production of helium during peacetime.

The Petroleum and Natural Gas Division is very largely a field organization and keeps only a small headquarters staff in Washington, D. C. Experiment stations are located at Bartlesville, Okla., and Laramie, Wyo. Field offices are maintained in Dallas, Tex., and Franklin, Pa., to conduct petroleum production research, and a field office and laboratory is located in San Francisc Calif. Field headquarters, engineering office, and experimental laboratory for the helium activities are maintained at the Amarillo Helium Plant, Amarillo, Tex. Other helium plants are at Exell, Tex., Otis, Kan., and Shiprock, N. Mex.

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H. C. Fowler, Petroleum Experiment Station, Bartlesville, Okla.
H. P. Rue, Petroleum and Oil Shale Experiment Station, Laramie, Wyo.
H. C. Miller, Petroleum Field Office, San Fancisco, Calif.
H. B. Hill, Petroleum Field Office, Dallas, Tex.
S. S. Taylor, Petroleum Field Office, Franklin, Pa.
C. W. Seibel, Bureau of Mines Helium Plants, Amarillo, Tex.

The material relating to petroleum and natural-gas research was correlated by H. C. Fowler. Almost all engineers and technicians of the Division have contributed directly or indirectly to the preparation of the report.

OIL AND GAS DEVELOPMENT AND PRODUCTION

A detailed program of research has been outlined by production engineers of the Bureau of Mines. The program includes the research aims of the Division and coordinates the various production research problems. Methods of attack have been outlined, and the importance of the problems has been evaluated so that the Bureau can render greater service to the petroleum and natural gas industry. For example, work on the flow of gas in large-diameter pipe lines and an investigation of the productivity of gas wells are problems of the research program that is already under way.

Production engineers and physical chemists at the Bartlesville station completed the work on the fluid characteristics of the Saxet, Tex., gas-condensate field. A report was published on a study of reservoir oils in Naval Petroleum Reserve No. 1, Elk Hills, Calif. Both were special war assignments which were comprehensive, providing fundamental information of lasting good to the petroleum and natural-gas industry. At the same time, work was done on long-range problems of a basic nature such as characteristics of gas-condensate fluids and reservoir oils. One report describing an apparatus for the study of gas-condensate fluids and four reports on internal corrosion in gas-condensate wells were published.

Characteristics of Gas-Condensate Fluids

Efficient utilization of the Nation's reserves of hydrocarbons contained in gas-condensate-type reservoirs requires a knowledge of problems not common to ordinary gas-producing operations. For a number of years an important part of the Bureau's work has been the study of two pressing problems associated with production from such reservoirs; the first, an investigation of fluid properties, and the second, finding a means of controlling corrosion. Operators need to know the composition, type, and characteristics of hydrocarbons, and physical behavior of the fluids contained in the reservoirs in planning methods of recovery. Gas-condensate fluids produced in many fields cause serious internal corrosion of well equipment, with the result that high

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maintenance costs are involved and a hazard to the safety of operating personnel is ever present. The Natural Gas Department of the American Gas Association and the Natural Gasoline Association of America have cooperated actively with the Bureau of Mines in investigations of these problems.

The studies of the characteristics of gas-condensate fluids have resulted in the publication of a number of reports covering a broad field. In general, they deal with such subjects as the properties of a fluid from a well, development of research equipment, means of combatting corrosion, and the many aspects of gas-condensate reservoir engineering.

Drawing on the results of 14 years of research on fluid characteristics, including studies made during World War II for the Petroleum Administration for War, a report[4/] was published that described 10 basic engineering problems in the recovery of gas-condensate fluids. As soon as an economically important reserve of gas-condensate hydrocarbons is discovered, solutions, at least tentative ones, must be found for a number of problems, including the following: (1) Size of the fluid reserve, (2) composition of the fluid and its richness in marketable hydrocarbons, and (3) the original phase state of the fluid in the reservoir. Depending largely on the size of the reserve and the phase state of the fluid in the reservoir, plans must be made for recovery of the hydrocarbons and answers must be found for questions relating to the following problems: (4) The progressive changes in the phase state of the reservoir fluid as pressure declines when fluid is withdrawn through producing wells, and (5) the effect of injected gas upon the phases of reservoir fluid under the practice of pressure maintenance and gas drive. The recovery of liquids that may exist in the reservoir involves the following problems: (6) The recovery of hydrocarbon liquids with lean reservoir fluids, including concepts of liquid saturation of the formation and flow of liquids through the formation, and (7) the recovery of rich gas-condensate fluids that may have critical temperatures in the range of reservoir temperatures and hence are in a single, liquid-like phase in the reservoir. Problems important to well operation but indirectly related to reservoir engineering are: (8) The determination of equilibrium factors for use in the design of equipment employed in extracting specific hydrocarbons from gas-condensate fluids, (9) the development and utilization of data on natural-gas hydrates to facilitate the operation of field collecting systems, gas pipe lines, and moisture removal plants, and (10) control of the internal corrosion of well equipment and gathering lines.

Operators, in developing procedures for the recovery of marketable hydrocarbons from gas-condensate reservoirs, have need for extensive knowledge of the phase relations of the fluids in the reservoir. To obtain this information experimentally for every reservoir would be expensive as well as time-consuming, with the result that many fields necessarily would be operated without

4/ Eilerts, C. Kenneth, Gas-Condensate Reservoir Engineering. Part I. The Reservoir Fluid, Its Composition and Phase Behavior: Oil and Gas Jour., Feb. 1, 1947, pp. 63-68; Part 2. Fluid Properties and Flow Relationships in the Reservoir: Ibid., Feb. 8, 1947, pp. 78-84; Part 3. Equilibrium Factors, Hydrates and Corrosion: Feb. 15, 1947, pp. 100-103.

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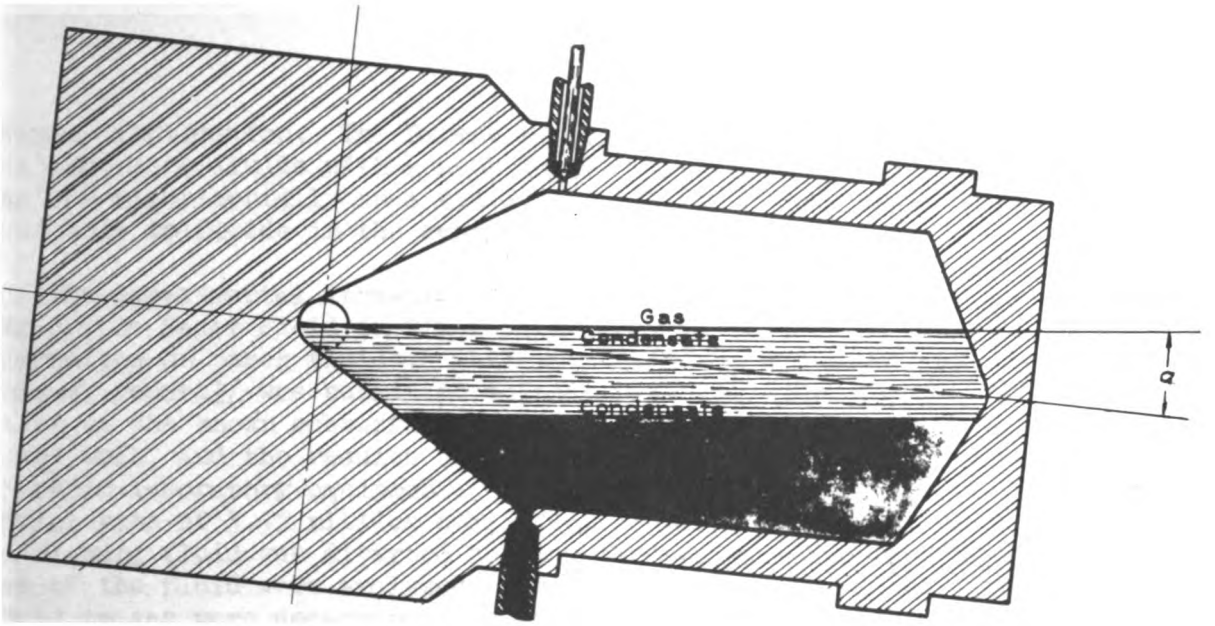
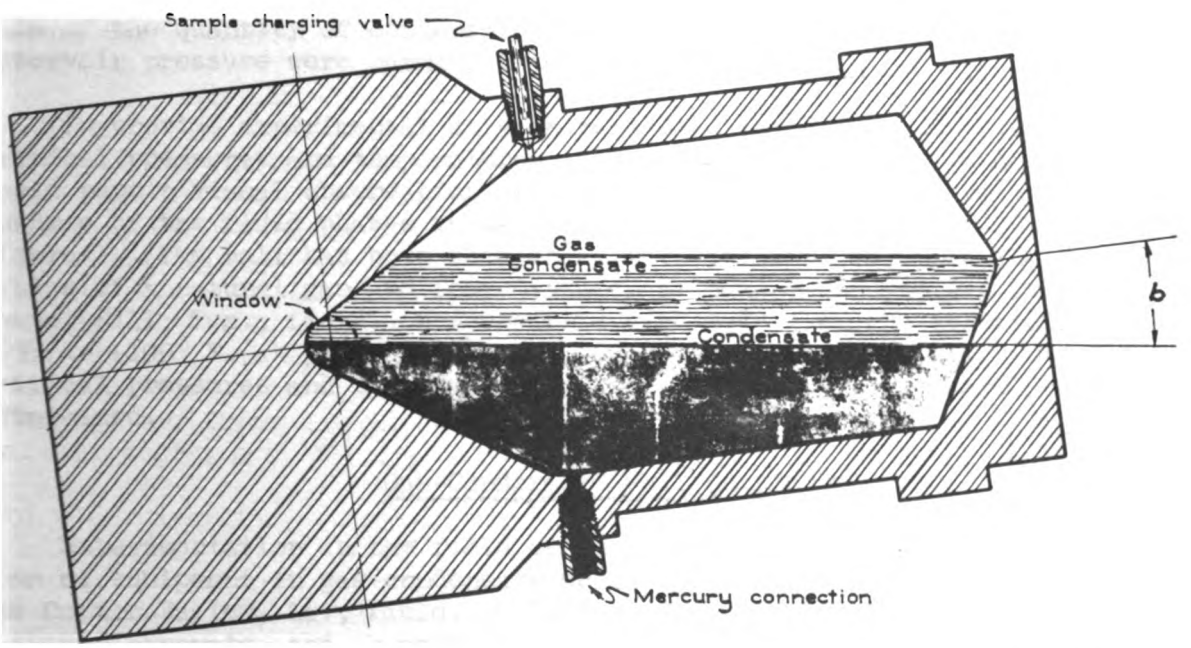


A.— Measuring Volume of Gas Phase



B.— Measuring Volume of Gas and Condensate Phases

Figure 1. - Use of windowed cell for measuring volumes of the fluid phases in equilibrium.

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adequate information. The Bureau of Mines has determined the properties of gas-condensate fluids with a high degree of accuracy so that the information obtained experimentally on a fluid from one field will be, in many cases, applicable to fluids in the reservoirs of other fields.

The experimental investigation of the properties of fluid from a reservoir in the Saxet Field in Texas is an example of a study designed to provide information on other fluids. This investigation was completed, and a preliminary report[5/] was submitted to the operators. The report includes information on the known subsurface geology of the reservoir, flow characteristics of the well, and the results of a study of the fluid properties made by means of mobile laboratory equipment. The test well was adjusted to flow at an average rate of 3.95 million cubic feet of gas a day, and a small portion of the flowing fluid was diverted to flow through portable test equipment. Samples of the fluid were analyzed to determine its composition. The ratios of liquid to gas were determined in the temperature range 86° to 280° F. and over the pressure range 450 to 3,200 psia. (lb. per sq. in. abs.). Dew-point pressures were determined at all test temperatures.

A phase diagram was constructed from the liquid:gas ratio data. As the reservoir pressure at the time of the tests was 3,042 psia., and the dew-point pressure at reservoir temperature (191° F.), experimentally determined, was 2,947 psia., the reservoir fluid was considered to be in a single gaslike phase in accordance with the concept of retrograde phenomena. Estimates were made of the quantity of condensate that would occur within the reservoir if reservoir pressure were permitted to decline.

To provide experimental data on relative liquid and gas volumes and critical pressures and temperatures, a windowed cell[6/] was constructed that would permit visual observation of fluid phases. The method of measuring the volumes of the fluid phases in equilibrium within the cell is illustrated in figure 1. The cell has been used to measure specific volumes and liquid:gas ratios of a natural gas and four mixtures of condensate and gas from the Chapel Hill, Tex., field. Measurements were made over the temperature range -65° to +100° F. at pressures up to 5,000 psia. Compressibility data and the critical pressures and temperatures of the gas and mixtures have been determined.

Gas-Condensate Well Corrosion

Experimentation in the field on the use of inhibitors to control corrosion of equipment in gas-condensate wells was continued at the test well in the Cotton Valley, La., field. Solutions of chromates (sodium chromate, sodium dichromate, and chromic acid) were pumped into the annular space of

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5/ Bureau of Mines, Engineering Report and Flow Characteristics and Properties of Fluid from the 6,900-Foot Sand, Saxet Field (East Extension), Nueces County, Texas, March 1947 (Preliminary).

6/ Eilerts, C. K., Barr, V. L., Hamontre, H. C., Bobrowski, F., and Mullens, N. B., Development of Windowed Cell: American Gas Association Monthly, Oct. 1946, pp. 435-440.

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the well, where they flowed to the bottom to enter the tubing with the hydrocarbon fluid from the producing formation. Decrease in the rate of metal loss from coupons exposed to the well fluid and lowering of the concentration of iron in the effluent water indicated the degree of corrosion control provided by aqueous solutions of the chromates.

Concurrently, laboratory tests were made of the resistance to corrosion of alloys and alloyed steels in corrosive media similar to those flowing in wells. To date, 95 alloys have been exposed for different periods of time to the corrosive action of propionic acid, carbonic acid, and phenol.

The field study showed that the chromates are effective inhibitors of corrosion in gas-condensate wells, and the results have been published.7/ The use of the chromates in the test well reduced the rate of corrosion of coupons exposed to well fluids from a pretest value of 0.045 to less than 0.005 i.p.y. (inches of uniform penetration of the metal per year). The concentration of iron in the effluent water was lowered from 100 to 4 p.p.m. (parts per million) or less. Where the inhibitor was in contact with the flowing fluid of the test well, some of the chromates were reduced to trivalent chromium compounds, which are insoluble in water. Under certain conditions, which are not completely understood, a part of the trivalent chromium compounds tended to become attached to the inner wall of the tubing near the entrance and form an obstruction that, if allowed to accumulate, lowered the flow capacity of the well. It was found that the accumulation of chromic compounds could be prevented and that previously formed obstructions could be removed slowly by maintaining a high pH (hydrogen-ion concentration) in the effluent water, keeping the chromate concentration in the flowing water low and injecting relatively large quantities of water into the well.

In every test, chromates were consumed (reduced) by the fluids of the test well. The results of a study, summarized in table 1, reveal that the quantity of chromates consumed is controlled by the pH of the water flowing with the fluid in the tubing. Sodium chromate used with sodium hydroxide produced a pH of 7.7 in the effluent water and was consumed at the rate of 1.21 pounds per million cubic feet of gas. With this treatment the flow capacity of the tubing was restored at the rate of 0.3 percent per day. Chromic acid, which provided a pH of 5.1 in the effluent water, was consumed at a rate equivalent to 2.67 pounds of sodium chromate per million cubic feet of gas. With this treatment, involving a relatively low pH, the flow capacity of the tubing was decreased at the rate of 0.4 percent per day despite the injection of water at more than twice the rates employed in the treatment providing a pH of 7.7.

7/ Ellerts, C. K., Carlson, H. A., Smith, R. V., Archer, F. G., and Barr, V. L., Sodium Chromate as an Inhibitor of Corrosion in Gas-Condensate Wells: Proceedings, Natural Gasoline Association of America, 1945-46, pp. 51-66; The Oil Weekly, Part I, Sept. 30, 1946, pp. 17-22; Part II, Oct. 7, 1946, pp. 30-34. Natural Gasoline Association of America Corrosion-Research Project Committee, Bureau of Mines Report: Minutes of Meeting, Oct. 17, 1946, vol. III, NGAA 21046, pp. 129-145; Jan. 23-24, 1947, vol. III, NGAA 4147, pp. 255-270; May 27-28, 1947, vol. III, NGAA 1547, pp. 327-342.

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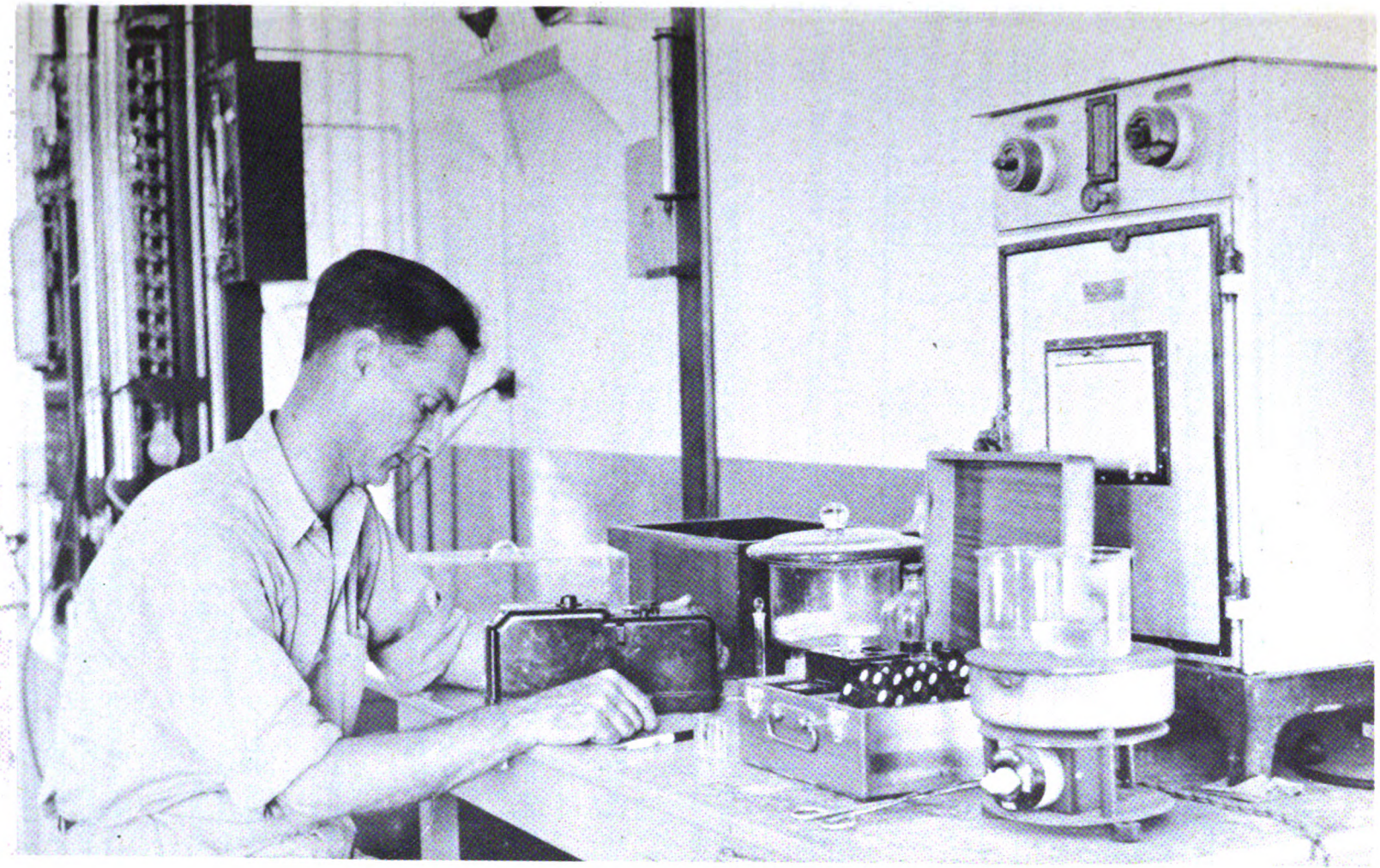

Figure 2. - View of field laboratory for analyzing properties of water from test wells.

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TAPLE 1. - Relation between the pH of the effluent water and the consumption of the chromates used in treating a gas-condensate well

Injected materials	Effluent water		Materials per million cubic feet of gas				
	pH	Iron content, p.p.m.	Water, injected, gal.	Sodium hydroxide injected, lb.	Chromate injected, lb.	Equivalent sodium chromate consumed, lb.	Coupon Corrosion, i.p.y.
Sodium chromate plus sodium hydroxide...	7.7	4	21.7	1.94	1.23	1.21	0.002
Sodium chromate.....	7.0	1	38.2	0	1.60	1.55	.001
Sodium dichromate...	6.4	0	45.6	0	2.30	2.36	.003
Chromic acid	5.1	4	55.1	0	1.65	2.67	.005

A view of the interior of the field laboratory, where analyses of the properties of the water produced from the test well were made, is shown in figure 2.

The search for a material resistant to the corrosion often found in gas-condensate well operation has led to testing 95 alloys and alloyed steels. The metal coupons were exposed for long periods to the corrosive action of propionic acid, carbonic acid, and phenol. The results of the study have been reported to the Corrosion Research Project Committee of the Natural Gas Association of America.8/

To be satisfactory for the manufacture of tubing for gas-condensate wells subject to corrosion, an alloy steel must meet these requirements:

1. High values of physical properties to withstand the pressures encountered in gas-condensate wells and to withstand the treatment the tubing receives in completing and repairing deep wells.

2. High resistance to the corrosive action of flowing gas-condensate fluids.

3. Economically practicable so that in use its cost is not excessive as compared with the cost of replacing carbon steel equipment as often as necessary or with the cost of treating wells with inhibitors or neutralizing agents.

The laboratory study of the corrosion resistance of alloys and alloyed steels has revealed that chromium steels are not more resistant to corrosion than carbon steels unless they contain 7.5 to 10 percent of chromium. Nickel steels must contain more than 8.5 percent of nickel to attain significant corrosion resistance. Copper-nickel steels are economical but do not show

8/ See footnote 7.

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promise as materials for equipment to be used in gas-condensate wells subject to corrosion. The copper-nickel steels are resistant to propionic acid corrosion but are much more susceptive to carbonic acid corrosion than are carbon steels. Figure 3 is a photograph of some copper-nickel coupons that have been exposed in carbonic acid. The stainless chromium-nickel steels and the chromium-nickel castings all showed favorable corrosion resistance.

Emphasis has been placed on determining the significance of the period of exposure in the testing of alloys for corrosive resistance. The metals are tested by exposures to the corrosive media for periods of 1, 28, 70 and 140 days. This is important, because it is not known when one of the tests most accurately simulates the conditions that prevail in corrosive wells. If a film of corrosion products is left to accumulate undisturbed on a metal surface exposed in a corrosive medium, the rate of corrosion of the coupon may change as the period of exposure increases. If the film is protective, the rate of corrosion will decrease with time; if the film is not protective, so that pitting may result, the rate of corrosion may increase with time. However, the film may not change the rate of corrosion, and metal losses then will be linear with time. Table 2 shows how rates of corrosion of several classes of metals are affected by the period of exposure.

TABLE 2. - Characteristic change in rate of corrosion with period of continuous exposure

Metals tested	Manner of rate change in indicated medium		
	Propionic acid	Carbonic acid	Phenol
Nickel steels	Increases	Linear	Linear
Chromium steels	Decreases	Linear	Linear
Copper-nickel steels..	Increases	Decreases	-
Copper-nickel alloys..	Linear	Linear	-
Low-carbon steels	Decreases	Increases	Indefinite

Petroleum Engineering Field Studies

Carthage Field

The Carthage, Tex., gas-condensate field, although discovered in 1936, developed during the war into one of the major natural-gas reserves of the Nation. The productive area is estimated to be 275,000 acres, with 244 completed wells (Jan. 1, 1947), of which 156 are dual completions producing from two formations and 88 are single completions. Over 170 billion cubic feet of gas had been produced from the field by January 1, 1947. Bureau engineers have completed the field work and have assembled cross sections, subsurface maps, and correlation sections describing the subsurface geology of the three principal gas-bearing formations, which are the Hill, Upper Pettit, and Lower Pettit.

New Hope Field

Engineers in the Dallas office have continued a formal study of the New Hope field, Franklin County, Tex. This field of 4,000 acres overlies one

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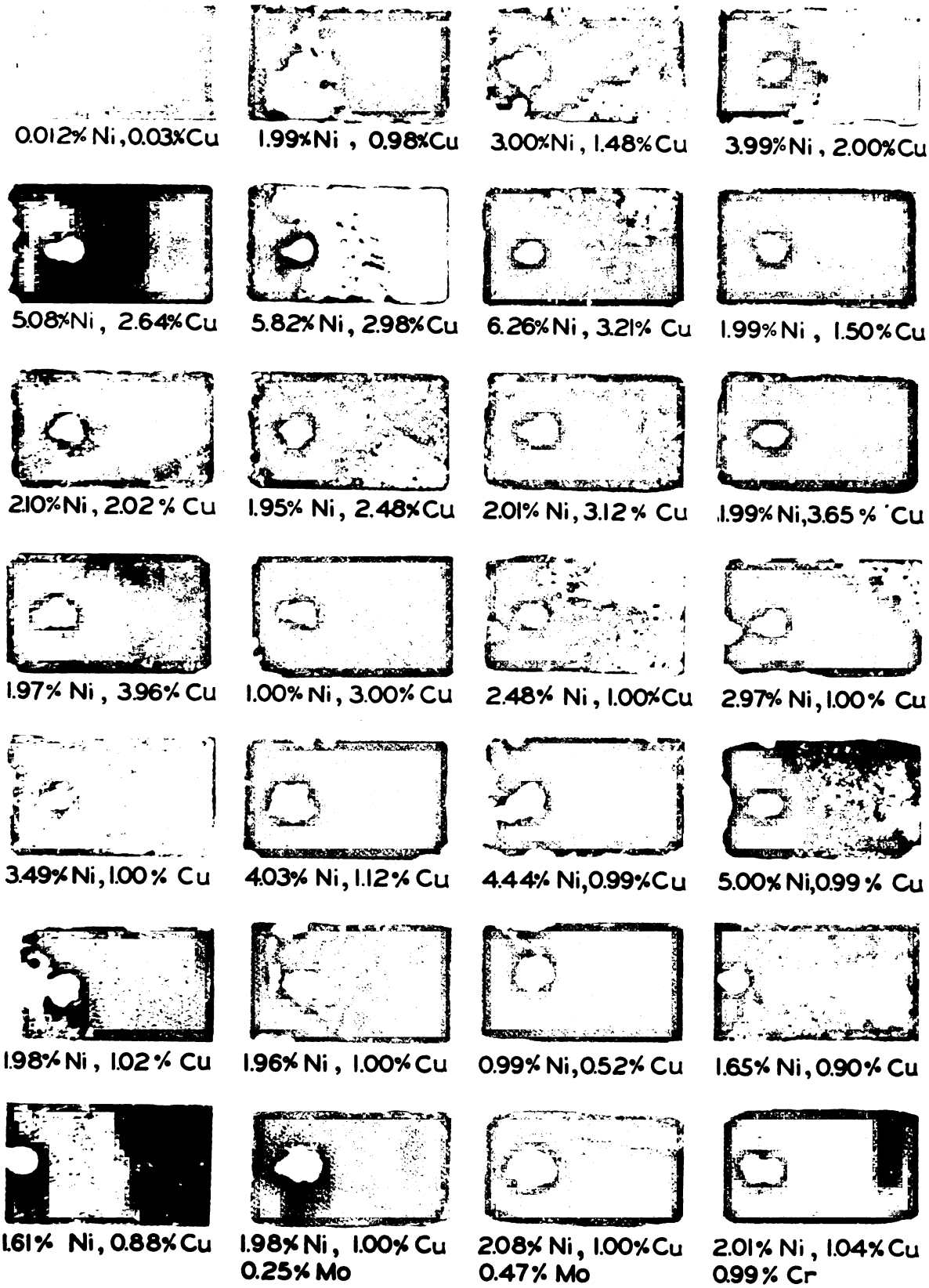

Figure 3. - Coupons of copper-nickel alloyed steels at conclusion of 98-day exposure test in aqueous solutions of carbon dioxide at 200 psia. and 130° F.

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limestone and three sandstone reservoirs, in which about 55 wells have been drilled. The crude oil in three of the reservoirs is undersaturated with gas, and the movement of edge water into the reservoirs is impeded by low permeability of the reservoir rocks. As the reservoir pressure in three reservoirs had declined sharply, and many wells have ceased flowing, it is apparent that the propulsive forces driving the oil to the wells is derived almost entirely from expansion of the reservoir fluids. Water is being injected into two reservoirs as a means of arresting the declines in pressure, but the low permeability also impedes the flow of extraneous water into the reservoir, and extremely high pump pressures are required at the surface for the introduction of relatively small volumes of water. As a result of this condition, the volume of reservoir fluids withdrawn exceeds the volume of extraneous fluids introduced, and the pressure continues to decline. Satisfactory progress is being made on the study, and a report should be completed during the next fiscal year.

Sheridan Field

A study of the Sheridan gas-condensate field was begun at the request of the Petroleum Administration for War. This study was continued after the war because of the general interest in deep-seated gas-condensate reservoirs and the probable importance of these reservoirs as future reserves of gas and liquid hydrocarbon. A report has been completed and will be issued shortly.

A number of dual completions in the Sheridan field have been reconditioned to produce only from one zone on account of corrosion, which has become a serious problem in this field.

The Sheridan cycling plant was designed to process 100 million cubic feet of wet gas daily from wells completed at depths of approximately 9,300 and 10,300 feet and to return about 80 million cubic feet of residue gas to the two principal gas-bearing zones at pressures of approximately 4,000 p.s.i. From August 1945, when the plant began operations, to March 1, 1947, 35.3 billion cubic feet of gas have been processed, from which 2.3 million barrels of hydrocarbon liquid have been recovered - an average recovery of 2.8 gallons per M cubic feet of gas. During this period, 30.8 billion cubic feet of gas have been returned through five input wells to the principal gas-bearing strata.

Lake Creek Field

The Lake Creek gas-condensate field in Montgomery County, Tex., was discovered in February 1941 by the Superior Oil Co.

The gas-producing section of the Wilcox formation in this field, between the approximate depths of 8,800 and 11,800 feet, has been divided into nine producing zones; each zone consists of one or more producing strata. The reservoirs in the field have been developed by 29 wells. A number of wells have been completed to produce from two or three zones through separate flow channels. The extremely low permeability of the gas-bearing strata (average 25 millidarcys or less) draws attention particularly to the flowing characteristics

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of the wells and pressure-production relationships, whereas the high hydrocarbon content of the wet gas (average 5.9 gallons per M cubic feet) offsets in part the relatively low initial production of gas and the monthly withdrawal from the individual wells.

The volume of gas treated from August 1943 to January 1, 1947, in the cycling plant erected in this field and designed to process 68.5 million cubic feet of wet gas daily was 39.5 billion cubic feet of gas, from which 5.6 million barrels of hydrocarbon liquid was recovered. During this period, 26.9 billion cubic feet of gas was returned to the producing reservoirs through five injection wells at a well-head pressure of approximately 4,100 pounds per square inch. Corrosion has not been a serious problem in the Lake Creek field.

The restricted report on the Lake Creek field, developed and prepared for the Petroleum Administration for War, has been brought up to date and revised in accordance with information revealed in drilling new wells. This report, containing 29 illustrations and 25 tables, will be issued as a Report of Investigations.

Rangely Field

Research regarding the characteristics of the Weber sand reservoir in the Rangely field, Colorado, and of the oil in that reservoir was continued. The results are providing the operators with information that will enable them to adjust oil-producing operations so as to obtain maximum economic recovery. The study also is providing data on the nature of the reservoir, although some of its characteristics are still undetermined. It has been determined that the oil in the Weber sand reservoir has characteristics that vary considerably from place to place, depending somewhat upon its position on the structure.

Special Problems of North Lindsay, Okla., Field

Following a plan of making studies of important newly discovered oil fields, the Bureau is investigating the physical properties of reservoir oil from the North Lindsay, Okla., field. The field lies on the edge of the Anadarko Basin, which is being subjected to an intensive drilling campaign and which is considered the most promising area for the development of future oil reserves in Oklahoma. Examination of subsurface samples from three oil wells has revealed the following unusual characteristics: (1) More than two barrels of oil are withdrawn from the reservoir for each barrel of oil collected in the stock tank, (2) approximately 2,500 cubic feet of gas is liberated from each barrel of oil produced into the stock tank, (3) the viscosity of the oil in the reservoir is less than that of water at reservoir temperature. The data indicated that the use of two gas-oil separators in series between the wells and the stock tanks will result in more than 3 percent greater oil recovery than the conventional single gas-oil separator. Because little is known of the physical properties of oils of the type found in the North Lindsay and adjacent reservoirs, the findings of the Bureau may play an important role in arriving at more efficient production practices.

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Plans have been made to furnish the industry with a preliminary report of the field and laboratory data on the North Lindsay field through publication in a trade journal.

Special Study of Reservoir Oils in Naval Petroleum Reserve No. 1, Elk Hills Field, California

At a request of the United States Navy, the Bureau of Mines, during the war, studied the reservoir oils from five wells in the shallow zones of the Naval Petroleum Reserve No. 1, Elk Hills field, California. Release of this information was obtained, and a report[9] has been published showing (1) pressure-volume-temperature and viscosity data of the reservoir oils tested, (2) correlation of some physical properties of the reservoir oils with A.P.I. gravities of the produced oils, and (3) application of material-balance concepts to a newly discovered oil reservoir that resulted in increasing the proved oil reserve and potential production of the field.

The material-balance equations[10] were applied to the reservoir in the Above Bittium sand discovered on May 1, 1945. Following completion of the discovery well, 82-2B, two offset wells were drilled - one to the east and one to the west of the discovery well. The Above Bittium sand was not found in either offset well, which led to the general conclusion that the reservoir penetrated by well 82-2B was a lenticular sand of limited areal extent. Accordingly, no further immediate plans were made to drill additional wells.

Knowing the physical characteristics of the reservoir oil as determined on the subsurface oil sample from well 82-2B, subsurface pressures and temperatures and the cumulative production of oil and gas made it possible to apply material-balance calculations to the reservoir content. These calculations showed a substantial source of reservoir energy. Consideration of the relation of the Elk Hills structure to the regional geology and the abnormally high initial reservoir pressure in the Above Bittium sand led to the conclusion that the indicated energy probably was not the result of an active water drive. Material-balance calculations then were made for the assumed reservoir conditions that the volume of oil removed from the reservoir was replaced (1) only by the expansion of the gas-saturated reservoir oil; (2) only by the expansion of free gas in the reservoir; (3) only by the expansion of water in the extraneous parts of the reservoir system.

It was found that the energy available from the expansion of either 274 million barrels of water, 6.5 million cubic feet of gas, 3.3 million barrels of oil or a combination of these volumes in the reservoir would provide the 12 p.s.i. decline in reservoir pressure resulting from the production of 8,260 barrels of oil. It was considered unlikely that the reservoir was large

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9/ Cook, Alton B., and Shea, G. B., Special Studies of Reservoir Oils in Naval Petroleum Reserve No. 1, Elk Hills Field, Calif.: Bureau of Mines Report of Investigations 4054, 1947, 60 pp.

10/ Cook, Alton B., Magnolia Oil Field, Columbia County, Ark. Derivation and Application of Material Balance Equations: Part II. Bureau of Mines Report of Investigations 3720, 1943, pp. 84-99.

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enough to contain water of sufficient volume to furnish more than a small portion of the energy. Furthermore, well 82-2B is near the axis of the Elk Hills anticline, and because the subsurface contours generally follow the major outlines of the surface structure it was concluded that if there were free gas it supplied only a small part of the reservoir energy.

As a result, Unit Operation decided to drill another well down-structure from well 82-2B. This well, 84-2B, was completed as a flowing well in the Above Bitt.ium zone on August 4, 1945. Subsurface conditions in the reservoir and the productivity of the offset well were similar to those of well 82-2B. This is an outstanding example of the application of engineering reasoning leading to a successful field operation that other wise might have been delayed for some time.

Correlation of Physical Properties of Oils

In continuation of the Bureau's long-range study to determine the relation between the physical characteristics of reservoir oils and the properties of oils as produced at the surface, data were collected from the Elk Hills, Calif., North Lindsay, Okla., Rangely, Colo., and New Hope, Tex., oil fields.

Examples of what may be accomplished by using correlations have been reported[11/] and are illustrated in figures 4, 5, 6, and 7, which show the relation between the A.P.I. gravities of produced oil and viscosity, oil density, compressibility, thermal expansion, volume of gas in solution, and shrinkage of the reservoir oils. The relationships may be used to estimate like properties of other oils in the same field within the gravity range without analyzing subsurface samples of the oils.

Data from the New Hope and North Lindsay fields are considered especially valuable in this study, as they have high A.P.I. gravities. Previously, only a few data on this type of oil were available.

Well-Spacing Studies

The oil industry and all consumers of its products stand to benefit from well-spacing investigations directed toward improved operation of oil-producing properties. Rising demands for nearly all petroleum products and existing or impending domestic shortages of many refined oils evince the seriousness of the present need for increasing recovery of crude oil from oil fields by continued research and application of technological advances.

Recognizing that the welfare of the public is concerned and that an industry-wide economy is related directly to their well-spacing studies, Bureau of Mines engineers have been making exhaustive theoretical and field investigations of various aspects of the well-spacing problem. Their goal is to find practical means for determining the minimum number of wells that should be drilled in oil fields to effect maximum oil recovery consistent with profitable operation.

11/ See footnote 9.

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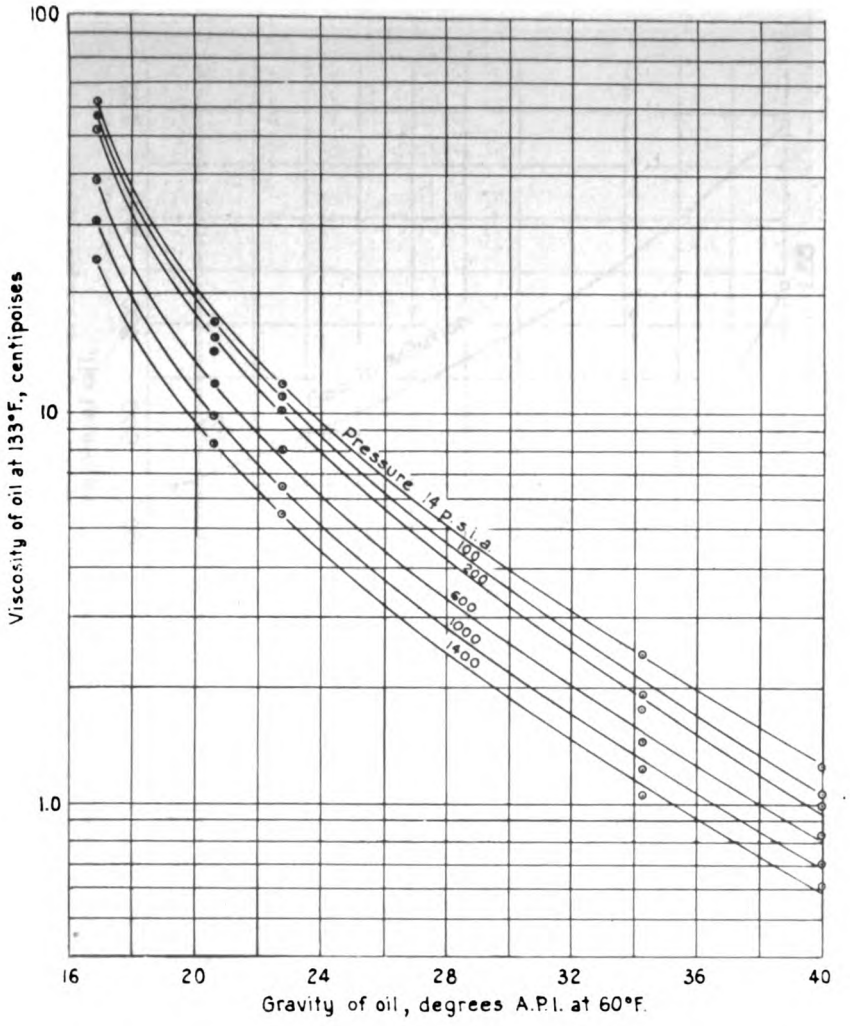

Figure 4. - Relationships between pressure-viscosities and A.P.I. gravities of produced oil, U.O.-N.P.R. No. 1, Elk Hills Field. Calif.

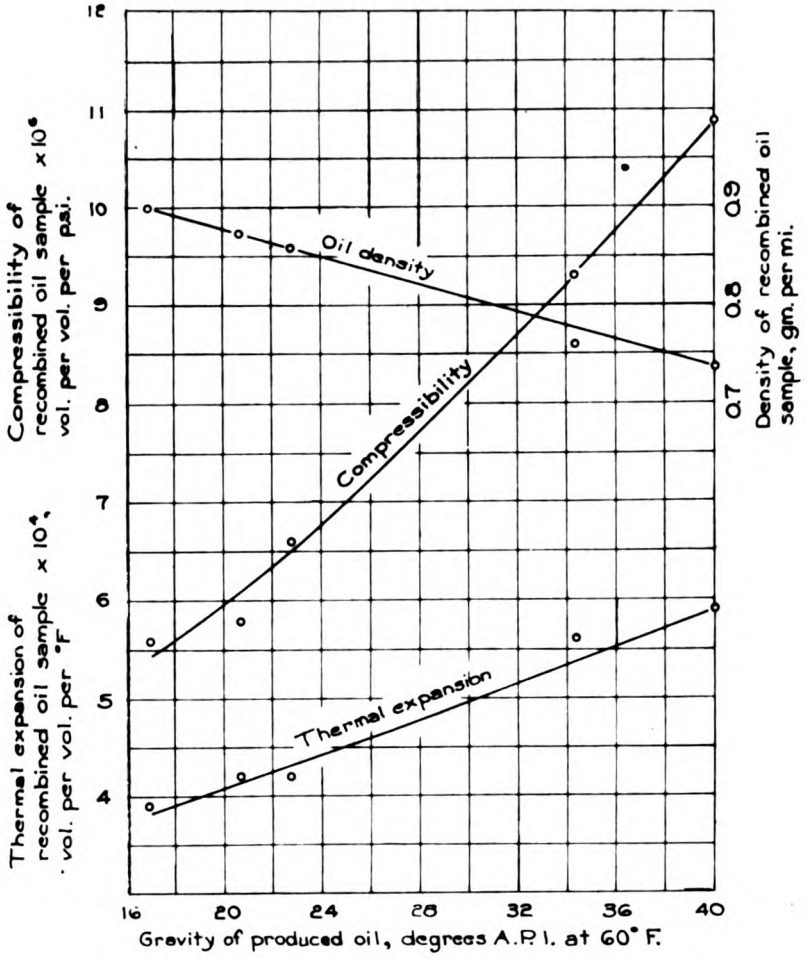

Figure 5. - Relationships between A.P.I. gravities of produced oil and oil density, compressibility, and thermal expansion of recombined oil samples at 1,400 P.S.I.A. and 133° F., U.O.-N.P.R. No. 1, Elk Hills Field, Calif.

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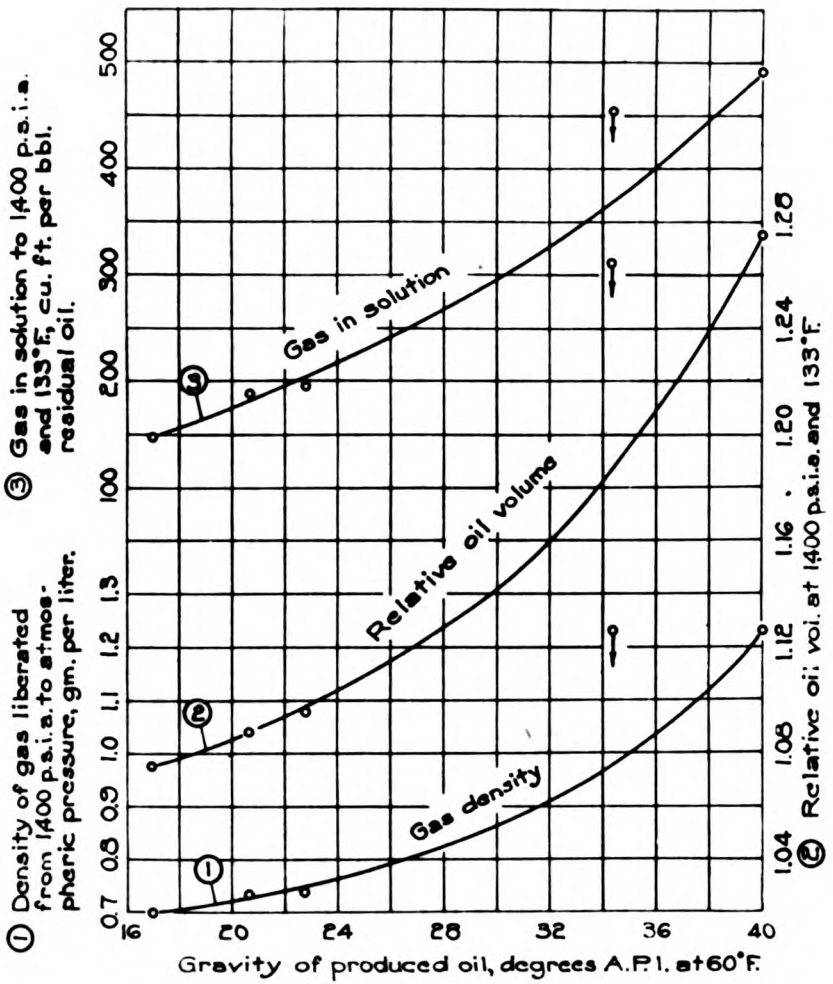
Gas in solution
Relative oil volume
Gas density
① Density of gas liberated from 1400 p.s.i.a. to atmospheric pressure, gm. per liter.
② Relative oil vol. at 1400 p.s.i.a. and 133°F.
③ Gas in solution to 1400 p.s.i.a. and 133°F., cu. ft. per bbl. residual oil.
Gravity of produced oil, degrees A.P.I. at 60°F.

Figure 6. - Relationship between A.P.I. gravities of produced oils and flash gas-liberation data, recombined oil samples, U.O.-N.P.R. No. 1, Elk Hills Field, Calif.

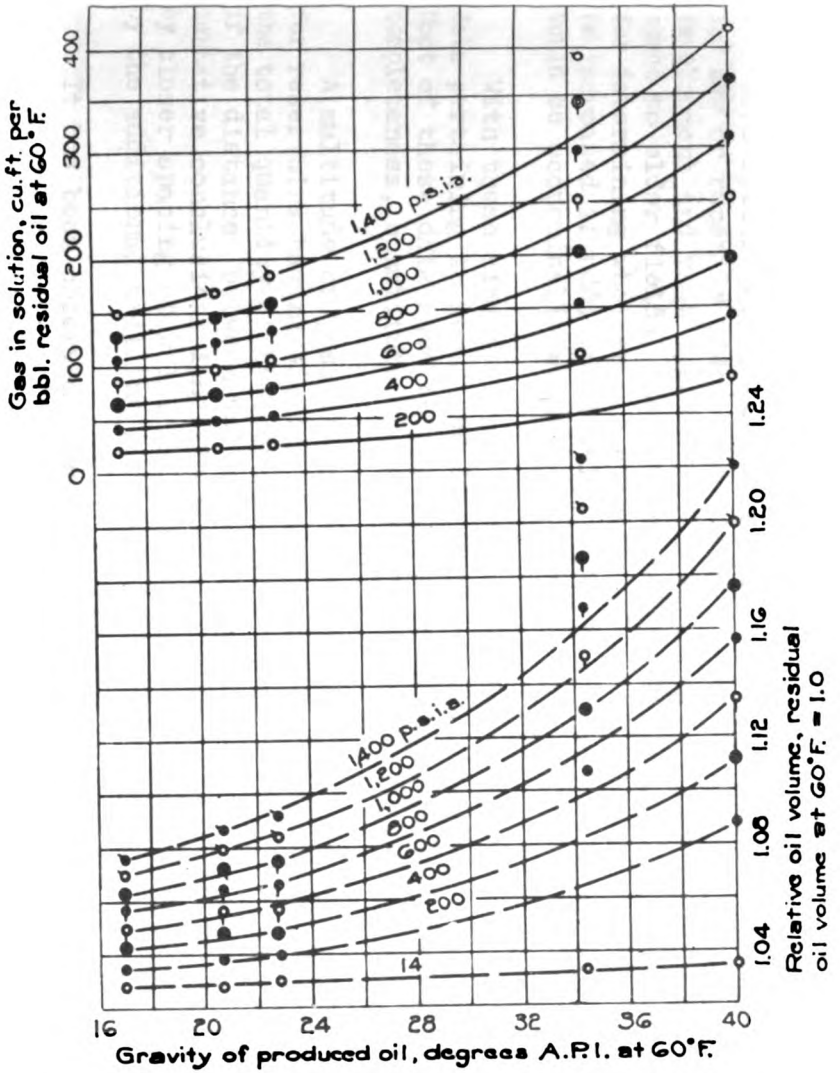

Figure 7. - Relationships between A.P.I. gravities of produced oils and differential gas-liberation data at 133° F., recombined oil samples, U.O.-N.P.R. No. 1, Elk Hills Field, Calif.

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More specifically, methods are sought whereby the optimum number of wells for new or recently discovered fields can be determined in advance of field development and then applied in the planning of drilling programs. With respect to older fields, the main objective is to develop methods of analysis for determining whether the quantity of petroleum yet to be recovered could be increased if additional wells were drilled, and whether such a venture would be economically sound.

With these aims in mind, Bureau engineers have been studying oil-field data pertaining to about 150 different fields throughout the United States. Most of these data have been published only recently and, because of their completeness, constitute an excellent source of basic information.

A multitude of possible correlations of field data have been attempted for reservoirs having similar characteristics. Thus far, it appears that the total quantity of recoverable oil from most types of reservoirs increases if the distance between wells is decreased. Significantly enough, however, tentative conclusions indicate that the probable gain in oil recovery caused by closer spacing of wells in many of the fields would be more than offset by the additional drilling costs and operating expenses.

It has been observed, further, that physical properties of crude oils affecting oil-recovery efficiencies possibly may be accounted for in terms of the A.P.I. gravities of the oils, and that oil-recovery efficiencies in general increase with the "lightness" (A.P.I. gravity) of the produced oils. If, for example, two fields could be identical in all respects except for the gravity of the produced oil, the field producing the lighter oil apparently should yield the greater quantity of oil.

It is expected that continued accumulation and analysis of field data will either substantiate the tentative conclusions already drawn or otherwise lead to a better understanding of relationships between well spacing and reservoir behavior.

Theoretical investigations based solely on physical and mathematical reasoning have been undertaken by Bureau engineers in an effort to develop explanations for tentative conclusions emanating from field studies. In this connection, no two fields are exactly alike, and thus conclusions premised on direct comparison between well spacing and estimated ultimate oil recoveries are always open to doubt, even for fields having similar characteristics. In contrast, it may be possible, through theoretical analyses, to determine, under idealized sets of conditions, the effect of various spacing intervals (distance between wells) on oil-recovery efficiencies. If, in this endeavor, the magnitude of various factors (excluding spacing intervals but including such entities as interstitial water content and permeability of reservoir rock) affecting oil-recovery efficiencies can be evaluated, then it may be possible to adjust field data properly before direct comparisons are made among similar fields regarding well spacing-recovery relationships.

In its well-spacing studies, the Bureau has maintained close liaison with the American Petroleum Institute Special Study Committee on Allocation of

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Production and Well Spacing, has worked with many oil-company engineers and officials vitally interested in the problem, and recently has established a relationship with a group of engineers in California studying the subject under the auspices of the Petroleum Division of the American Institite of Mining and Metallurgical Engineers.

Studies of the Effect of Drilling Fluids Upon Core Analysis

Knowledge of the quantities of oil and water present in a reservoir sand is necessary for determination of oil reserves and evaluation of oil property. Efficient operation in recovery of oil from petroleum-bearing reservoirs is based upon an accurate knowledge of the quantities of oil, gas, and water present in the reservoir. This knowledge is no less important in secondary-recovery problems, which are increasing in the oil industry as the end of the flush production of many of the country's large oil fields is approached.

When cores are cut from a petroleum-bearing formation with water-base drilling fluids, some water usually filters from the drilling fluid into the formation, displacing reservoir fluids. Consequently, the cores recovered at the surface contain not only an unknown amount of drilling-fluid filtrate but also only part of the oil and water that was in the formation before the hole was drilled. For that reason, the results of analysis of cores cut under such conditions do not show the true picture of the reservoir fluid contents. Consequently, engineers usually are compelled to make a rough estimate of the relative percentages of oil and water in most reservoir sands.

The Bureau of Mines, in cooperation with the American Petroleum Institute and several oil companies, is carrying out a series of tests to find improved methods for measuring the degree of contamination of cores by drilling-fluid filtrates. In these tests, cores are cut with an oil-base drilling fluid, because filtrate from this fluid is known by test to penetrate porous formations less than the filtrate from water-base drilling fluids. A tracer is added to the oil-base drilling fluid, so that a quantitative measure can be made of the volume of filtrate that enters the cores. The tracer is an organi chloride that is insoluble in water, highly soluble in oil, very stable at high temperature, and not easily vaporized. Samples of the drilling fluid are obtained while the cores are being cut, so that the concentration of the tracer in the filtrate from the drilling fluid can be determined and the volume of the filtrate per unit weight of tracer calculated.

Although such fluids were in the bore hole, cores were cut from a well in the South Coles Levee field, California, and the Rangely field, Colorado. At the wells, the cores were cleaned of drilling fluid and sealed in tin cans, care being taken to minimize any loss of vapors from the core samples before the cans were sealed. These cores were taken to the laboratory, where, in addition to the customary core analysis, approximately 300 determinations of tracer content were made. Detailed measurements of the properties of the drilling-fluid samples have been made. Now that nearly all of the field and laboratory procedures have been completed, analysis of the data has been started. After the data have been analyzed, a report will be prepared for publication.

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SECONDARY RECOVERY

Increased interest in secondary recovery of oil and the part it must play in the future of the petroleum industry and the country as a whole was evidenced in many quarters during the year. The following statement by Paul D. Torrey, national chairman, Secondary Recovery Committee, American Petroleum Institute, to the Secondary Recovery Forum in Washington, D. C., May 15, 1947, is typical of many made during the year:

> I desire to emphasize the magnitude of the problem which confronts us. Certainly, great progress has been made in recent years in the development of methods for increasing oil recovery, but there remains much yet to be done. We still need to expand our sights and think in terms of literally billions of barrels of unrecovered oil, which might mean the difference between victory or defeat should our country become involved in another war which might eliminate the availability of foreign sources of crude supply. Surely this is a matter of such vital importance that we should be condemned severely if we do not adopt every measure in our power to insure an adequate crude reserve for the possible future needs of the United States.

The increased interest in secondary recovery was responsible for numerous requests from the general public, trade associations, and trade journals for results of Bureau of Mines secondary-recovery studies and for information about the work. An article[12/] describing briefly several projects on which work is in progress was prepared for one of the trade journals. Bureau engineers worked closely with numerous other agencies interested in stimulative methods of oil production, including the Interstate Oil Compact Commission, the American Petroleum Institute, the Pennsylvania Grade Crude Oil Association, the North Texas Oil and Gas Association, and others. An extensive bibliography[13/] covering all articles on secondary-recovery methods of oil production is prepared annually for the Secondary Recovery Committee of the American Petroleum Institute.

Methods of Increasing the Recovery of Oil

Field Studies

The Bureau of Mines has published histories of water-flooding in Illinois, Kansas, and Oklahoma. The latest of this series, dealing with water-flooding in north Texas,[14/] was published in July 1946. In Texas, water flooding has

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12/ Taliaferro, D. B., Secondary Recovery Research of the Bureau of Mines: Independent Monthly, vol. 17, No. 6, October 1946, pp. 15-18.

13/ Taliaferro, D. B., 1943-1945 Supplement to the A.P.I. Bibliography on Secondary Recovery of Oil: Proceedings, Twenty-fifth Annual Meeting American Petroleum Institute, sec. 4, Production Bull. 231, November 1945, pp. 15-28.

14/ Grandone, Peter, Jessup, D. A., and Taliaferro, D. B., History of Water Flooding of Oil Sands in North Texas: Bureau of Mines Report of Investigations 3906, July 1946, 117 pp.

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been limited largely to the old "shallow" fields of the north-central part of the State in an area extending south through Wichita and Clay Counties, on the Red River, into Brown County. The projects center mainly in two oil-producing districts known as the Burkburnett-Wichita Falls District in Wichita County and the Olney-Prideaux District in Young County.

The injection of water into oil-bearing formations through selected wells to stimulate production at other wells began on a systematic basis in Texas in 1936 with a small experimental project in Brown County. By 1940, seven initial projects in three counties had demonstrated the practicability of the method in the north Texas "stripper" fields, and by the end of 1944 the practice had extended into five additional counties.

A total of 38 water-flooding projects, covering 1,970 acres, was undertaken in the first 8 years of water flooding in Texas, each of which is described in the published report. A total of 1,141,000 barrels of oil was recovered from these projects by the injection of 12,062,000 barrels of water. Report of Investigations 3906, describing these operations, has been in demand since it was released, and its second reprinting was ordered in June 1947.

In November 1946, the Bureau of Mines, in cooperation with the North Texas Oil and Gas Association, opened an office in Wichita Falls, Tex., to make field studies and to do other work that will be of assistance to operators of secondary-recovery projects in that area. Because of popular demand, the first undertaking of the personnel assigned to the Wichita Falls office was to prepare a supplement to the earlier report[15/] on the history of water flooding in north Texas. Many of the necessary data were collected, and the report was being written as the fiscal year closed.

D. B. Taliaferro and R. K. Guthrie prepared a paper[16/] for the annual secondary-recovery meeting of the North Texas Oil and Gas Association, which briefly reviewed the results that had been obtained on 11 typical water-flooding projects in north and north-central Texas. Figure 8 shows graphically the results obtained on one of the outstanding projects described in the report. This project includes only 25 productive acres, on which there were 13 old wells when water flooding was initiated. Only two new wells were drilled. The shaded area on the figure represents 72,000 barrels of oil estimated to have been recovered over and above that which would have been produced to the end of 1946 had pre-flood production methods been continued. Extrapolation of the production-decline curve indicates a probable ultimate recovery by water flooding in excess of 4,700 barrels of oil per acre.

...A type of work that is of great value to operators initiating secondary recovery projects is the engineering study of selected fields suitable for the application of secondary recovery methods. Such a report[17/] was published

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15/ See footnote 14.

16/ Taliaferro, D. B., and Guthrie, R. K., Results of Water-Flooding Oil Sands in North and North-Central Texas: Producers Monthly, vol. 11, No. 5, March 1947, pp. 15-26.

17/ Johnston, Kenneth H., and Riggs, C. H., Secondary-Recovery Practices and Oil Reserves in the Eastern Part of the Delaware-Childers Field, Nowata County, Okla.: Bureau of Mines Report of Investigations 4019, December 1946, 50 pp.

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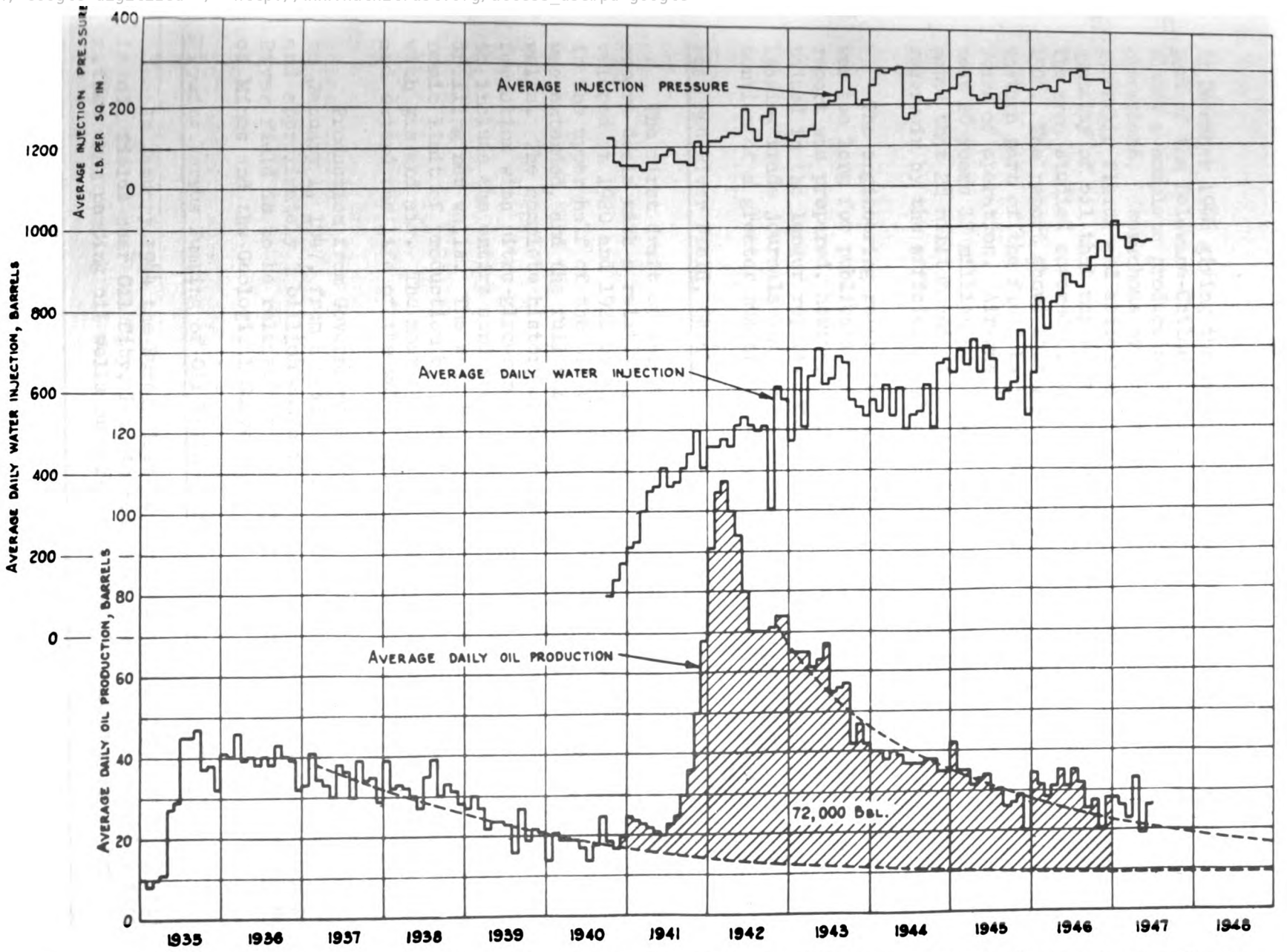

Figure 8. - Production history of White & Duncan, J. S. Webb water-flooding project, Archer County, Texas.

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in December 1946 giving the results of an extensive study of the eastern part of the Delaware-Childers field in Nowata County, Okla. The report includes a complete production history, a study of existing secondary-recovery operations, isopachous or sand-thickness map, sand-contour maps, analyses of reservoir fluids and estimates of the oil reserves left in the sand, and the quantity of oil that may be recovered by systematic, efficient water flooding. The area studied covered 6,800 productive acres that were first developed in 1906. The report shows that 23 million barrels of oil were produced from the eastern part of the field by primary production methods during the first 20 years of operation. Air-gas injection was initiated in 1925, and during the next 20 years 17 million additional barrels of oil was recovered. It is estimated that 28 million additional barrels of oil can be recovered from the reservoir by the efficient application of water flooding.

The engineering report on the eastern part of the Delaware-Childers field was too long for publication by the trade journals. A condensation[18/] of the report was prepared, however, which contained many of the important data contained in the longer report. The shorter report was published by one of the leading trade journals and served to bring the results of the study to the attention of a greater number of secondary recovery operators.

West Red River Field, Oklahoma

The first draft of the West Red River report has been prepared. This report deals with a relatively small lenticular sand field that was first developed in 1920 and 1921 by 31 wells. These early-drilled wells were bottomed in the upper half of the oil-producing sand section. At a later date the field was extended, and the full reservoir section was developed by deepening the wells. The complete history of this field centers largely around shooting the formation with nitro-glycerin to increase production, deepening the old wells to include the entire sand section, vacuum operations, repressuring, and drilling new wells. The West Red River field virtually has reached the economic limit of production by primary and secondary methods of repressuring with gas and air. The most favorable method remaining to increase production and extend the life of the wells probably is water flooding.

Production from Government-supervised leases in the West Red River field to January 1, 1947, from a maximum of 61 wells was 6,903,000 barrels of oil and approximately 7 billion cubic feet of gas. The study of the West Red River field is to be released as a joint report by the engineers of the Bureau of Mines and the Geological Survey.

Flowing Versus Pumping of Oil Wells on Air-Gas Injection Projects

In January 1944 the Bureau initiated research involving experimentation in oil fields near Oil City, Pa., to reduce to practice (if feasible) flowing rather than pumping oil wells on air-gas injection, secondary-recovery

18/ Johnston, Kenneth H., and Riggs, C. H., Secondary-Recovery in the Delaware-Childers Area: Oil Weekly, vol. 125, No. 11, May 12, 1947, pp. 57-58, 60-62, 64.

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projects. The production method was found practical and has proved popular among operators. Numerous local flowing installations followed the initial one, affording the Bureau the opportunity to use real oil wells and fields in its studies on the applied research phase of the program. To date one report[19] has been published.

The initial objective of this study was to devise means to siphon-flow intermittently rather than to pump intermittently the oil produced on air-gas injection projects, utilizing the energy inherent to the gas accompanying the oil into the well bore to flow the oil to the surface rather than to dissipate most of the energy in the gas, as customarily practiced when pumping the wells. This study has now crystallized into four separate but related parts, each of which will be the subject, eventually, of one or more publications: (1) An investigation to determine the feasibility of flowing the oil produced on air or air-gas injection projects, (2) laboratory research on factors affecting the design of flowstrings (siphons), (3) study of the effects of gas- or air-gas-injection rates and pressures upon oil-recovery rates and ultimate recovery, and (4) investigation of air- or gas-injection operations where restoration of reservoir pressure and flowing of the oil wells are being practiced. All four parts of the flowing investigation are being carried on simultaneously, but the first has reached the stage where manuscript writing has been initiated.

A 10-foot laboratory model of a well designed to investigate the fundamental characteristics of siphon flow through small-diameter pipes was rebuilt during the year to improve the accuracy of experimental results. The model consists of a "well" made of plastic tubing 2 inches in diameter with plastic tubes of various diameter used as flowstrings. There are tanks containing the oil used in the experiments with auxiliary manometers, gas-oil separator, gas meter, pressure regulator and valves to control and indicate the flow of oil and air through the apparatus. During the year the model has been operated to obtain fundamental data only as time permitted from field work. The operation of the model has been conducted mainly to verify observations made in the field of flowing wells in which siphons, whose designs were based on laboratory data previously obtained with the model, are in operation. Fundamental data on siphon-type flowstrings were obtained, however, on 1/4-inch and 1/2-inch tubes with various numbers and sizes of orifices. Most of the experiment have been conducted in the range of 30 percent and higher submergences in order to determine the most efficient characteristics of the flowstrings studied.

19/ Grant, Bruce F., and Bossler, Robert B., Experimental Flowing of Oil Wells on Air Injection Projects in Pennsylvania: Petroleum Engineer, vol. 17, No. 11, July 1946, p. 103, 104, 106, 1 fig.; Oil Weekly, vol. 122, No. 7, July 15, 1946, p. 38, 40, 42, 1 fig.; Producers Monthly, vol. 10, No. 9, July 1946, p. 38, 40, 41, 42, 1 fig. (The same report was published under the title "Experiments on Flowing Oil Wells in Venango Field Watched with Interest; May Cut Costs:" The Blizzard Newspaper, Oil City, Pa., vol. 102, No. 62, August 3, 1946, p. 1 and 9.)

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A fundamental relationship has been found between the number and size of orifices in relation to the diameter of the flow tube. In later experiments it has been learned that the number of orifices did not matter, provided the total cross-sectional area of the orifices was the same. The relationship has been reduced to a ratio between the total cross-sectional area of the orifices to the cross-sectional area of the flow tube. The size of the orifices used in field installations is a factor only in that too small an orifice is likely to plug with wax or encrustations from mineral waters produced with the oil.

Experiments during the latter part of the year were confined mainly to those wherein the submergence ratio was below 30 percent even though the efficiencies are lower than for the previous experiments. Many field installations operate with submergence less than 30 percent. To date, all of the fundamental relationships proved in the laboratory have been applied successfully to field practice. For example, several siphon flowstrings installed in wells failed initially to produce oil by flowing. After the ratio between orifice size and flow-tube diameter was corrected, as indicated by laboratory data, the wells flowed properly.

Submergence is the length of a static column of well liquid that is equivalent to the gas pressure in the annulus between the flowstring and the casing or well bore at the point of gas entry to the flowstring. For convenience, submergence has been reduced to a simpler term - "percentage submergence," which is the ratio, expressed as a percent, between the submergence and the total length of the flowstring above the orifices. Thus, in practice, if one knows the closed-in wellhead pressure, the oil, water, and gas production rates, and the depth of the well, a siphon flowstring 1,100 feet long, or less, ordinarily can be designed in accordance with the relationships between percentage submergence and the jet:flowstring area ratio data obtained in experiments with the model well and verified in the field.

As soon as the fundamental relationships between additional sizes of small-diameter pipes are ascertained, the experiments will be devoted to determining the relationship that exists between all of the factors proved to date and the length of the flowstring. The length of the flowstring is the one factor that has not been taken into consideration in the laboratory work. Because of the shortness (10 feet) of the "well," it is not known whether these characteristics can be determined with this piece of equipment. If they cannot be, a longer tube installation will be utilized.

Oil-Well Reconditioning in the Appalachian Region

The reconditioning of oil wells is one of the most important problems confronting operators in the Appalachian region, because the wells are old and the gas pressure initially in the reservoirs has been virtually depleted. In areas where secondary recovery operations have not been initiated, reconditioning of the wells is the most promising means of maintaining their productive lives. It has been estimated that less than 15 percent of the wells in the Appalachian region are influenced by secondary recovery methods. Consequently, the remaining approximately 114,000 wells depend for their survival

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on profitable operation, which requires sustained production rates maintainable mainly by periodic clean-out procedures.

For several years engineers of the Franklin office have been studying oil-well reconditioning in the Appalachian region. Oil-well reconditioning as practiced in the Appalachian region is essentially a clean-out operation. Statistical data on such operations have been accumulated over a period of years, and analyses have been made. A report[20] on this work was completed during fiscal 1947.

The report is an engineering statistical analysis of the results of clean-out operations on 366 wells from the vicinity of Pittsburgh, Pa., to the southern extremity of West Virginia and in southeastern Ohio. This report on reconditioning results and methods in use in southern Appalachian fields is particularly timely, as there are a large number of wells in dire need of clean-out because of increased operating costs and inflexible price structure imposed during the late war. The productive sands in the area studied occur at depths ranging from 1,000 to 3,000 feet, so that redrilling in connection with secondary recovery development necessarily will be limited, and the future of oil production in these fields is directly dependent on keeping the existing wells in operation.

In addition to studying clean-out methods and procedures, an effort was made to determine the actual increased oil production attributable to clean-out jobs by analyzing the production history of each of the 366 reconditioned wells. A study of the 1,058 clean-out jobs disclosed that the average cost was $895, and thirty-eight 8-hour days of rig time were required to complete it. Production was 29 barrels of oil per month for the average well before cleaning and 67-1/2 barrels of oil per month after cleaning. The increased production of 38-1/2 barrels per month cost $23.25 per increased barrel of oil per month. For comparison, it was estimated from figures published during the past 7 years by the West Virginia Department of Mines on initial oil production of new wells in West Virginia, and the assumption that it cost $12,000 to drill and complete a well, that each new barrel of oil per month cost $25.60. On this basis, the economics of clean-out work compares favorably with new drilling as a means of increasing oil production in West Virginia.

Efficient Rates and Pressures of Injection

Although water flooding has been practiced for about 25 years, there still is much to learn about the mechanics of the process. There is no agreement as to the most desirable injection rate, although it is generally agreed that there is a maximum pressure that may be applied on any reservoir without damage to the sand. Excessive pressures cause cracks to form in the sand, through which most of the injected water will flow to nearby oil-producing wells. Very little work has been done in some water-flooding areas to determine what maximum pressure can be applied safely, and only a few operators in

20/ Grant, Bruce F., Oil-Well Reconditioning in Southwestern Pennsylvania, West Virginia, and Southeastern Ohio: Bureau of Mines Report of Investigations 4193, 1948, 82 pp.

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these areas have made tests to determine how their input wells are performing. A study of this important problem was initiated by Bureau of Mines engineers. Many tests are being made on water-input wells to find the maximum limits of pressures and rates. These will be followed by other tests to determine the pressures and rates that will give the most efficient recovery of oil from the reservoir.

Selective Plugging

Oil reservoirs are made up of porous rock formations that almost always consist of numerous strata of widely differing permeabilities. In the secondary recovery of oil by water flooding or by gas injection, the most permeable sections are flushed of their recoverable oil first. Those strata from which a large percentage of their producible oil has been swept take fluid at the input wells and produce it at the oil wells at increased rates, while the strata of low permeability may still retain most of their producible oil.

A study was initiated of methods and materials that might be used to plug selectively the most permeable parts of the sand after the recoverable oil has been removed. Numerous experiments were made in the laboratory on well cores with emulsions of asphalt and resin as the plugging media. These materials appear to be suited for this purpose, and arrangements are being made for field tests.

Core and Water Laboratory

A report was published21/ describing a method developed in the Bureau of Mines laboratories for the determination of the oil and water saturation of oil-field cores. The method has been adopted by several core-analysis laboratories. It has been found to be simple and yet unusually accurate, and the necessary equipment may be purchased at a reasonable cost. The necessary technique may be acquired easily and quickly.

The determination is made by extraction and measurement of loss in weight, using a modification of the A.S.T.M. apparatus for the determination of water in petroleum products. The core sample is crushed to fragments 1/4 inch or less in diameter and is placed in an alundum thimble that has been oven-dried and weighed. The thimble and contents are weighed, and the thimble then is placed in the neck of a flask designed to support it above the solvent in the body of the flask. Toluene is a suitable solvent, although others might be used. A water trap and condenser are fitted to the flask, and the entire assembly is placed on a hot plate. The water is distilled from the test sample and collects in the graduated trap, where its volume may be read directly. The refluxed solvent returns to the flasks through the porous thimble until all the oil has been extracted from the sample. The porous thimble then is removed from the flask and dried in an oven. The volume of oil in the sample is calculated from the known gravity of the oil and the loss in weight of

21/ Rall, Cleo Griffith, and Taliaferro, D. B., A Method for Determining Simultaneously the Oil and Water Saturations of Oil Sands: Bureau of Mines Report of Investigations 4004, December 1946, 16 pp.

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the sample after making allowance for the weight of water as computed from the volume of water removed from the sample. The report describing the method includes a complete working drawing of the apparatus, a photograph of a battery of 12 units used in the Bureau's Bartlesville, Okla., laboratory, a description of the apparatus, the procedure used, sample calculations, and an analysis of the precision of the method.

Standard mineral analyses of 138 oil-field brines were made by the Bureau's laboratory at Bartlesville, Okla., and 210 core samples were tested during the fiscal year. Special tests made on some of the oil-field brines included determination of hydrogen-ion concentration, carbonate stability, total dissolved iron, hydrogen sulfide content, the optimum hydrogen-ion concentration for the precipitation of magnesium and the proper chemical treatment to obtain chemical stability. Laboratory personnel assisted in sampling and preserving several cores at the well site. A new technique employed on one core taken in the Mexica field, Texas, involved quick freezing of the samples with dry ice to prevent alteration of their oil and water content until they could be transported to the laboratory for analysis.

Several years ago a cooperative arrangement was entered into between the Franklin office and the Petroleum Section of the Pennsylvania Geological Survey in which the Bureau of Mines agreed to analyze the cores taken by the Survey under a special study set-up by the Pennsylvania Geological Survey and financed by special grant of the Pennsylvania Legislature to study oil sands in Pennsylvania. During the past year two core analyses were made for the State organization. One was obtained from a well in Butler County and the second from a well in McKean County, Pa. The results of these core analyses made by Bureau technicians will be published by the Pennsylvania Geological Survey in subsequent reports.

During the year, laboratory work was done in an effort to develop an oil-base mud that would be suitable for cable-tool coring operations in the Appalachian region. The major portion of the cores taken of reservoir formations in the region are cut with Baker tools utilizing standard cable-tool practice. As a general rule, water is used as the drilling fluid, and oil and water saturation determinations made on these cable-tool cores have been unsatisfactory. Usually the oil saturation is lower and the water saturation higher than those representative of the formation. An effort is being made by Bureau engineers to ascertain data utilizing oil-base mud that will be more representative of the saturation conditions of reservoirs. The laboratory tests were confined to developing a mixing technique and the specifications of an oil-base mud of proper filtration characteristics. A premixed oil-base mud was purchased to expedite the application of oil-base mud to cable-tool coring in the Appalachian region. Operators interested in the development and application of oil-base mud to cable-tool coring have offered wells for testing during the summer of 1947. It is anticipated that this work will provide comprehensive data that will indicate the applicability of oil-base mud to cable-tool coring in various oil sands in the Appalachian region. This work should contribute greatly in efforts to obtain cable-tool cores containing fluids more representative of reservoir conditions.

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Recovery of Wax from Crude-Petroleum Wastes

The pilot plant near El Dorado, Kans., for the recovery of oil and wax from crude petroleum wastes was closed and dismantled upon the successful conclusion of this work. A technical paper describing the method of treatment and the results of the pilot-plant operation is being prepared. The report will present in detail a discussion of the successful process, describing fully the equipment, method of operation, results obtained, and the analytical procedures used in the control of the process and in testing the reclaimed oil. One chapter will relate to a microscopic study of oil field waste and the physical character of the wax recovered from it. This section will be illustrated with colored photomicrographs. The preliminary laboratory experiments conducted in the development of the process and the early operational difficulties will be summarized.

Laboratory Study of Gravity Drainage and the Effect of Temperature

With the completion of gravity drainage of oil from the miniature oil field described in the previous year's report, the oil sand was cored in accordance with a uniform pattern to determine the residual oil saturation throughout the formation. The results of the core analyses showed that the residual oil saturations were low (10 percent) at the top of the sand and increased gradually with depth; near the bottom of the sand the saturations increased rapidly to a maximum (60 to 70 percent) at the base of the formation.

A study of the thermocouple readings taken during the application of heat to the tunnel in the latter stage of the experiments shows that the mean temperature throughout the formation was increased 13°, 20°, and 35° F. when the temperature in the tunnel was, respectively, 50°, 100°, and 150° F. above the original temperature (84° F.) of the formation. In other words, owing to the radial characteristics of the flow of heat from a small tunnel into a large formation, the mean temperature of the formation was increased only one-fourth of the temperature increase in the tunnel. The results of the temperature study show that the increase in mean temperature throughout the sand body was not enough to reduce the viscosity of the oil so as to increase drainage of the oil through the sand. However, in those parts of the sand adjacent to the tunnel the temperatures were markedly increased, and the oil saturations were found to be lowest where temperatures in the sand were highest, thus showing that heat increased drainage by reducing the viscosity of the oil and decreasing the influence of capillarity through lowering the surface tension of the oil.

Recovery of Oil from Outcropping Bituminous Sandstones by Hot-Water Washing

The bituminous-sandstone problem continued to receive major emphasis in the investigations of the Production Section of the San Francisco office. The previous year's report contained an account of the development in the laboratory of a method of separating the bitumen from the bituminous sandstones of the Edna deposit in San Luis Obispo County, Calif. The work of the past year consisted in improving the efficiency of the process and studying operating

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procedures for the purpose of obtaining separated bitumen end-products adaptable for fuel oils having certain standard specifications.

Significant increases in the efficiency and economics of operation of the laboratory pilot plant were achieved by (1) reduction of the power cost and loss of bitumen to slimes by the use of lower speed of the impellers in the flotation cells, (2) elimination of expensive reagents that were used previously as dewatering and desilting aids, (3) development of a diluent and froth mixer in which the diluent is dissolved in the bitumen without turbulent motion, and (4) the elimination of one of the pulping agents, with an appreciable reduction in cost, if the separated bitumen is to be cracked to coke.

In view of the increasing demand for petroleum products, consideration was given to the use of the bitumen extracted from the Edna deposit as fuel oil with little or no additional processing. The results of tests designed to establish the suitability of the separated bitumen for fuel oil showed that under carefully controlled plant operations the diluted bitumen end products met the specifications for No. 6 fuel oil (Bunker C), including viscosity, sediment by extraction, water by distillation, and flash point. The fuel oils thus obtained required only the removal of small quantities of water by distillation to conform to standard specifications.

Plant procedures also were designed in which fuels conforming to the specifications of No. 6 fuel oil could be obtained by removing the diluent from the separated bitumen and reducing the viscosity of the remaining bitumen by light cracking. The essential requirement in these operations was to obtain a bitumen for cracking having a silt content low enough to meet the specification test for silt. Thus, if the economics were such that it would be desirable to recover the diluent from the separated bitumen, the remaining bitumen would meet the sediment-by-extraction test. and the other specifications could be met by breaking the viscosity of the bitumen.

The bitumen also may be converted to other products by cracking. One cracking test yielded 17 percent of liquid fractions in the boiling range of gasoline, 20 percent gas oil, 21 percent heavy fuel oil, and 40 percent residuum.

Fundamental Research

While conducting the work described in the foregoing sections, Bureau of Mines technologists have dealt in much exploratory thinking regarding improvements that must be made in the Nation's productive capacity from the known sources of supply. It is their conclusion that conventional methods of water flooding and gas repressuring must be augmented by other means developed through research in order to offset the difficulties that now beset the effort to maintain adequate reserves of crude oil. Even in those areas where water flooding has reached its highest degree of efficiency, there still remains much oil in the sands after the flood has passed.

For many years technologists have done fine work on the physical properties of petroleum (liquid and gas). Bureau engineers and chemists and those

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in industry have studied properties such as the solubility of gases in petroleum, viscosity, capillarity, and adhesion, as well as the porosity and permeability characteristics of reservoir rocks. Thinking now is directed to the view that these properties and others should be given additional consideration on a fundamental basis so as to shed more light on their effect upon the propulsion of oil from the sands and how and why oil is retained in the sands. The Bureau's technologists are unaminous in their view that to obtain generally higher recovery efficiencies, studies must be made soon to determine the interfacial relations of the oil, water, and solid materials constituting the reservoirs. Outstandingly important among these phenomena is that of interfacial tension between two substances (such as oil and water or oil and sand) and the sifnificance of this property in oil production. Here is where research must concentrate.

PETROLEUM CHEMISTRY AND REFINING

Post-war considerations in 1946 led to the statement that "the current broad objective of the research in petroleum chemistry and refining is to obtain a complete picture of the availability of fuels for all types of internal-combustion engines. This includes motor and aviation gasolines, Diesel fuels, and gas turbo fuels." During 1947 there has been no change in this stated objective of petroleum chemistry and refining research. In fact, the work underway and contemplated has been planned on the assumption that this objective would continue over a considerable period of years.

The various phases of the work pattern designed to attain the desired objectives are so interlocked that it is difficult to set up independent categories for discussion. However, the four topics given below offer a suitable basis for discussion:

I. Raw-material studies (at present confined largely to crude oil, but may also include condensates and synthetic fuels)

II. Relationships of fuel composition, properties, and performance

III. Utilization of petroleum products

IV. Analytical methods

Raw-Material Studies

Crude Oils

A study of fractions from 10 selected crude oils, started in 1946, was completed, and the information was compiled and reported to the industry in a paper presented at the Regional Meeting of the American Chemical Society at Kansas City.22/ This report reviews the method by which the fractions were

22/ Holliman, W. C., and Smith, H. M., Composition of Petroleum: Hydrocarbon Type Analyses of 10 Distillates Boiling Between 100°-600° F.: Presented at Regional Meeting, Am. Chem. Soc., Kansas City, June 23-25, 1947.

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made and their properties determined, tabulates all of the determined and calculated properties and shows graphically the composition of the fractions in terms of paraffins, mono- and dicyclic naphthenes, and mono- and dicyclic aromatics. A companion paper, which discusses the development and application of correlations between the routine data and other special properties as reported in the previous paper, has been completed. The relationships studied, which have resulted in various types of graphical or mathematical correlations, include those between kinematic viscosity and specific gravity of routine analysis fraction; sulfur content of crude oil and sulfur content of distillates obtained from the crude oil; boiling range by routine crude-oil distillation and by ASTM distillation; aromatic content and specific gravity of routine analysis fractions; aromatic content and specific dispersion of routine analysis fractions; and aniline point and specific gravity.

These correlations greatly enhance the usefulness of the Bureau of Mines routine analytical method, which has been employed consistently for about 25 years, with the result that many hundreds of analyses are available for study, and the data obtained in the two papers mentioned above are being used in evaluating distillates of certain boiling ranges prepared from U. S. crude oils. Thus, the correlations developed and others upon which work is still going forward will be used in estimating the yield of indicated properties of distillates of the following boiling ranges:

a. 100°-300° F. F-3 octane No. clear and with 4 ml. TEL.

b. 100°-550° F. Sulfur, aromatics, viscosity at -40° F. and 100° F., freezing point.

c. 300°-480° F. Sulfur, aromatics, viscosity at -40° F. and 100° F., freezing point.

d. 350°-675° F. Sulfur, Diesel index, freezing point.

e. 675°- up Furol viscosity at 122° F., gravity, sulfur, carbon residue.

Without having such correlations, an immense amount of work would be required to obtain the same data experimentally.

During the current year, two reviews of United States crude oils were prepared. One was a summary of crude oils of importance during the period 1935 to 1945.[23] This report, which will be published as a part of volume V of the Science of Petroleum, presented data on almost 300 crude oils of the United States and detailed analytical data on about two-thirds of this number. These analytical data included not only a summary of the routine analysis but also correlated data obtained during the war period showing the aviation gasoline base-stock content, the toluene and C_7-naphthene content of many of these crude oils, and detailed hydrocarbon analyses of nine naphthas in the boiling

23/ Smith, H. M., Characteristics of United States Crude Oils 1935-45: Science of Petroleum, Oxford Press. In press.

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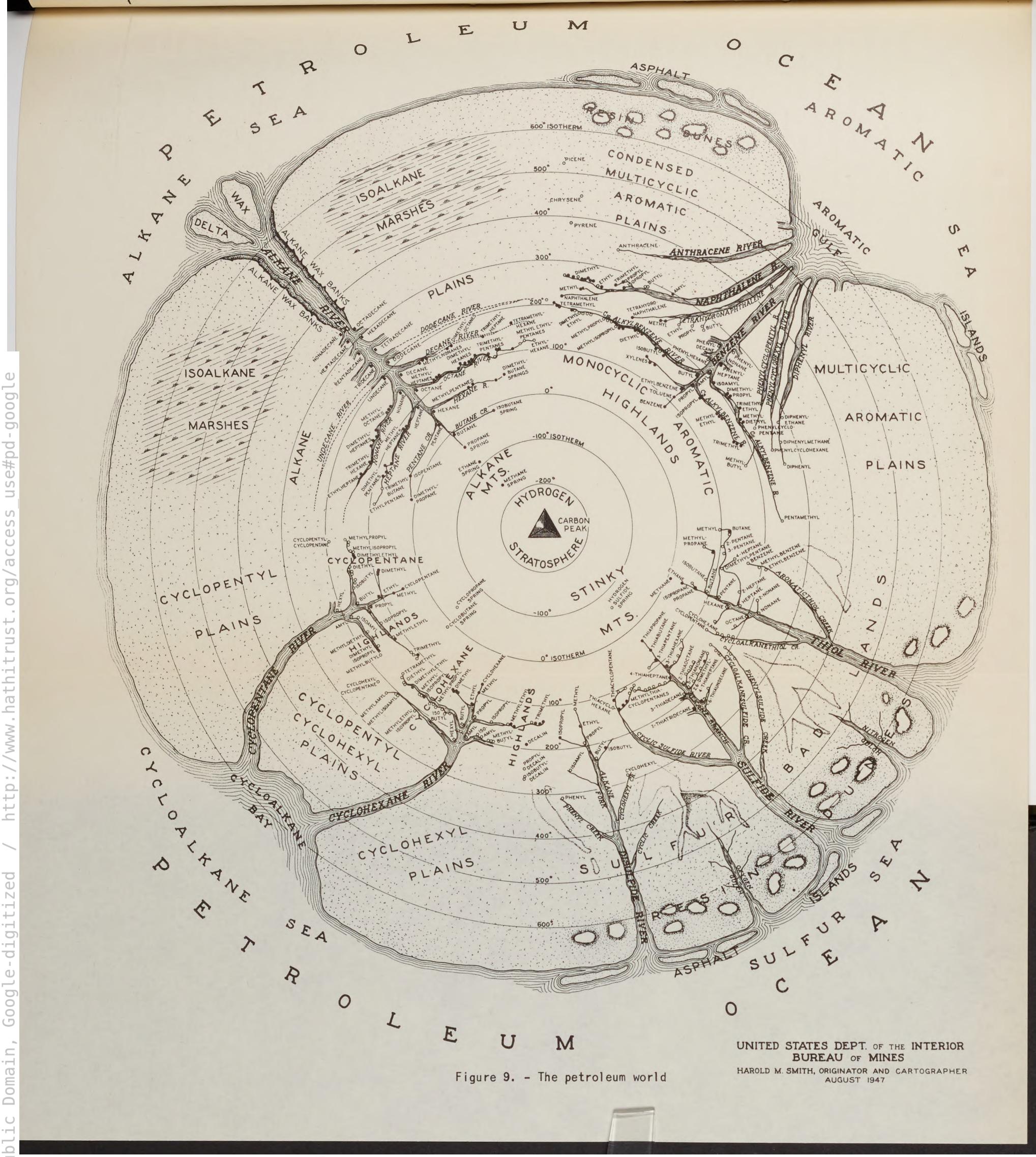

Figure 9. - The petroleum world

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range 97°-243° F. The other report,[24] dealing with United States crude oils, was prepared for presentation at the Chemical Research Conference of the American Association for the Advancement of Science. This report discussed the following questions: What is crude oil? Where is crude oil found? What is the composition of petroleum in terms of commercial products? What is the composition of the naphthas and gas oils produced by straight-run distillation from United States crude oils in terms of hydrocarbon type? What is the sulfur content of United States crude oils? Are there any relationships between hydrocarbon types and between individual hydrocarbons as they exist naturally in crude oils? In this report a map (fig. 9) called The Petroleum World has created considerable interest. It is an attempt to present pictorially in one chart an interpretation of current knowledge on the composition of petroleum. The concept of the map is simple. In the center is the carbon atom (called the Carbon Peak) surrounded by a stratosphere of hydrogen. From combinations of these two elements stem all the hydrocarbons. Concentric rings, which are isotherms in °C., extend from the hydrogen stratosphere at the temperature of liquid hydrogen to over 600° C. The map is further divided into quadrants, in which can be plotted, at their proper boiling points, the hydrocarbons and sulfur compounds present in crude oils. One quadrant is for the alkanes, a second and third for the naphthenes and the aromatics, and, finally, the fourth for the sulfur compounds along with oxygen and nitrogen compounds. Compounds that have been identified in crude oil are shown by solid circles, other compounds that may be present by open circles.

For convenience, each quadrant is discussed separately.

Alkane quadrant. - The alkanes are relatively simple to picture. They consist only of straight-chain compounds progressively increasing in size by a $-CH_2$ increment and of isomers of each of these various sizes and numbers of side chains. It will be noted that most of the alkanes through the octanes have been identified in petroleum, but above the octanes, except for the n-alkanes, only a few of the many possible isomers have been positively identified. The frontier here covers the region 150°-200° C. Virtually nothing is known of the higher-boiling isoalkanes. In fact, their existence in petroleum is one of the petroleum chemist's intriguing mysteries. The alkanes, therefore, may be portrayed as a single large river with many tributaries rather systematically spaced. This river empties into the alkane sea through the wax delta at the mouth of the river and eventually into the petroleum ocean.

Aromatic quadrant. - The picture of the aromatics is greatly different from the alkanes. As the map shows, this area contains many rivers, all emptying into the aromatic gulf. The benzene river is the largest and has many tributaries among its alkyl derivatives. There are, however, many other rivers, such as naphthalene, anthracene, and tetralin streams in the condensed nuclei land, and phenylcyclopentyl, phenylcyclohexyl, and diphenyl rivers in the conjugated ring area. In some respects the aromatics seem to be better

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[24] Smith, H. M., Composition of American Petroleum: Presented at the Chemical Research Conference. Am. Assoc. Adv. Science, June 30-July 4, New London, N. H.

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known than the alkanes; possibly because of the earlier research on coal tar. However, even here the frontier does not extend beyond the 200° C. isotherm, except for isolated cases. Offshore islands of asphalt are shown adjoining resin dunes on the main shore all along the aromatic quadrant. This indicates the essentially aromatic character of the resins and asphalts, although present knowledge of them is fragmentary.

Naphthenic quadrant. - Only the cyclopentyl and cyclohexyl types have been found in petroleum. The naphthenes are, therefore, represented by two major rivers - the cyclopentyl and the cyclohexyl - both with alkyl tributaries and both emptying into cycloalkane bay. Only a very few of these naphthenes have been identified in crude oil. This is especially distressing, because, as will be shown later, 85 percent of the gas oils contain more than 50 percent naphthenes, and even in the naphtha range 75 percent of the naphthas have 30 percent or more of naphthenes. Virtually nothing is known about the conjugated derivatives of dicyclohexyl or the alkyl derivatives of decalin. Also, the polycyclic naphthenes above the decalins should be shown, but there are few data regarding them. They may be assumed to be present in the plains area. The frontier on naphthenes is just barely on the 100° C. isotherm. These facts certainly indicate the need for concerted studies on the naphthenes.

Heterogenous quadrant. - In this quadrant the sulfur compounds are of chief interest. There seem to be three major types - the thiols or mercaptans, the sulfides, and the disulfides. The thiophenes are excluded, as at present there is no evidence that they actually exist in petroleum prior to processing. The sulfur compounds are complicated by the fact that all three of the hydrocarbon types can be represented. Thus, in addition to the main river of alkane thiols, there are aromatic and cycloalkane thiol creeks. Similar situations exist as regard the sulfides and disulfides, and in addition there are the cyclic compounds in which the sulfur is a part of the ring. The available knowledge is very meager, and the frontier is hardly at the 100° C. isotherm. Resin dunes along the shore and offshore asphaltic islands again are shown to indicate the importance of sulfur, oxygen, and nitrogen in material of these types. Oxygen and nitrogen streams are shown, but there are not enough data to warrant the placement of any definite compounds. Although considerable work on nitrogen compounds has been done, there is some doubt whether those identified were present in the original crude oil or represent decomposition products.

This map has been discussed rather fully in this report because it indicates the reasons for the present orientation of the chemistry and refining work. Thus, the dearth of knowledge in the Diesel fuel boiling range, from 200° C. to 400° F., is very evident, as is the tremendous void in the knowledge of sulfur compounds. Also, the importance of naphthene chemistry on the utilization of petroleum products emphasizes the need for analytical methods that will enable their determination.

In discussing the topics where is crude oil found and what is its composition, the author of the report considered fields producing 5,000 barrels or more per day, the locations of which were shown on maps. The basic data

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from the work on 10 selected crude oils previously referred to[25] were used in combination with the relationship of correlation index[26] to composition, thus permitting the estimated paraffin, naphthene, and aromatic contents of gasolines and naphthas prepared from these crude oils to be presented by means of bar graphs. The sulfur content of crude oils from various parts of the country was also shown by suitable graphs. Finally, the paper closed with a discussion and figures indicating that there are definite relationships between the various individual components in a given class of hydrocarbons; that is, fairly definite ratios appear to exist between the normal hydrocarbons in the range C_6 through C_9, between the isoparaffins in the same range, and between the various individuals in these hydrocarbon types and in others, such as the naphthenes and aromatics. There do not appear to be relationships between definite classes, such as the naphthenes, paraffins, and aromatics. These data are very important from several points of view and will be the subject of a separate paper during the coming year.

One Report of Investigations covering routine analyses of Louisiana crude oils was published.[27] This, the fifth of a series of papers dealing with Louisiana petroleum reports data on 82 samples from both northern and southern Louisiana.

During the last 10 or 12 years the Bureau of Mines has worked with a research committee of the Tulsa Geological Society attempting to find relationships of characteristics of crude oils and their stratigraphic occurrence. In 1947, an article[28] appeared in the bulletin of the American Association of Petroleum Geologists discussing such relationships for parts of Oklahoma and Kansas. The data presented are based almost entirely upon Bureau of Mines routine analyses and the correlation index,[29] and the results suggest most strongly that the environment of the source material may have determined the kind of oil in each oil pool. This work, which is of interest to geologists, chemists, and engineers, is being continued to cover other parts of Oklahoma and Kansas.

Virtually all of the references to crude oils thus far have dealt with their composition and means by which it can be determined from various types of analytical data. Many of the crude oils discovered in the last few years have had a high content of sulfur, which causes difficulty both in refining and in utilization of products. For this reason, the Bureau investigated the

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25/ See footnote 22.

26/ Smith, H. M., Correlation Index to Aid in Interpreting Crude-Oil Analyses: Bureau of Mines Tech. Paper 610, 1940, 34 pp., 4 figs.

27/ Blade, O. C., and Garton, E. L., Properties of Louisiana Crude Oils. III. Additional Analyses, Bureau of Mines, Rept. of Investigations 4034, Dec. 1946, 50 pp.

28/ Tulsa Geological Social Research Committee, Relationship of Crude Oils and Stratigraphy in Parts of Oklahoma and Kansas: Bull., Am. Assoc. Pet. Geol., vol. 31, No. 1, January 1947, pp. 92-148.

29/ See footnote 26.

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possibilities of desulfurizing crude oil directly by contact with a catalyst. A series of crude-oil desulfurizations with bauxite catalyst were made at 750° F. with a liquid hourly space velocity of 1/3 to 1 and with total charges of 1 liter, 3 liters, and 5 liters, respectively, to 2,400 ml. of bauxite. Crude-oil desulfurization is more complex than naphtha desulfurization, because in addition to sulfur removal, there is a conversion of heavy residual material to light material; also, there are losses from gas formation and from a heavy carbonaceous deposit on the catalyst. Complete material balances were made for each of these runs, and the products were distilled into gasoline, gas oil, and residuum. Selected tests were made on each of these cuts.

The bar graph in figure 10 shows the weight percent of each cut from untreated Slaughter crude oil and from corresponding cuts from the 1-, 3-, and 5-liter runs. Selected properties are shown for each cut. A Report of Investigations covering this study is virtually completed.

A bulletin, to consist of several parts and tentatively entitled "Routine Crude Oil Analyses," has been begun under the authorship of N. A. C. Smith and H. M. Smith, with chapters by others. Part 1, detailing the procedures and equipment for routine analyses, has been carried through the rough-draft stage by O. C. Blade and E. L. Garton, and considerable work has been done on Parts II and III, which will deal with interpretation of the analytical data. This bulletin will bring to date information on routine crude-oil analyses which was originally presented in Bulletin 207,30/ now out of print. Several thousand samples of crude oil have been analyzed by this method, and most of these analyses have been published from time to time, beginning with Report of Investigations 2202 in 1921.31/ The fundamentals of this method have not changed, although laboratory procedure has improved as apparatus more suitable for the purpose has become available and a number of additional tests have been added. Therefore, analyses published as early as 1921 are comparable with those made in recent years.

A report to be issued as an information circular, tentatively entitled "Bibliographic List of Reports Showing Analyses of Crude Oils by the Bureau of Mines Routine Method," is in preparation. In addition to the bibliography, a table is included showing by field name, according to continent, country, and (for the United States) State, the analyses represented and the reports in which they have appeared. This table will serve as a finding list for the analyses, which total well over two thousand.

The unprecedented peacetime demand for gasoline, coupled with the growing use of Diesel fuel, has aroused much interest in routine analyses of crude oils from new fields, formations, and from areas not extensively sampled during previous years. During the past fiscal year, the Bureau made 100 complete

30/ Dean, E. W., Hill, H. H., Smith, N. A. C., and Jacobs, W. A., The Analytical Distillation of Petroleum: Bureau of Mines Bull. 207, 1922, 82 pp., 3 pls., 33 figs.

31/ Dean, E. W., Properties of Typical Crude Oils from the Eastern Producing Fields of the United States: Bureau of Mines Rept. of Investigations 2202, 1921, 51 pp.

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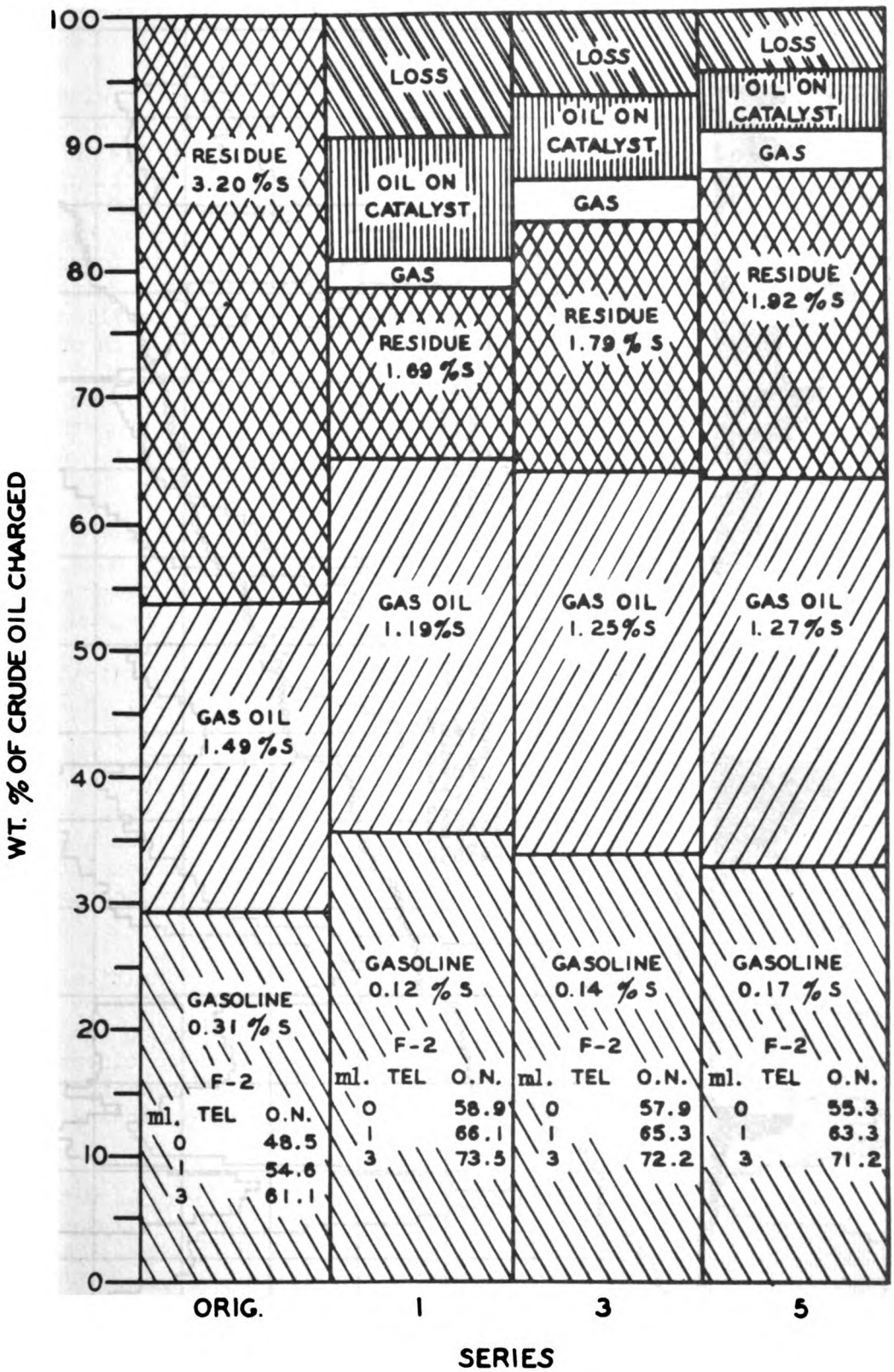

Figure 10. - Chart showing quantity and quality of distillate obtained from Slaughter crude oil by bauxite desulfurization.

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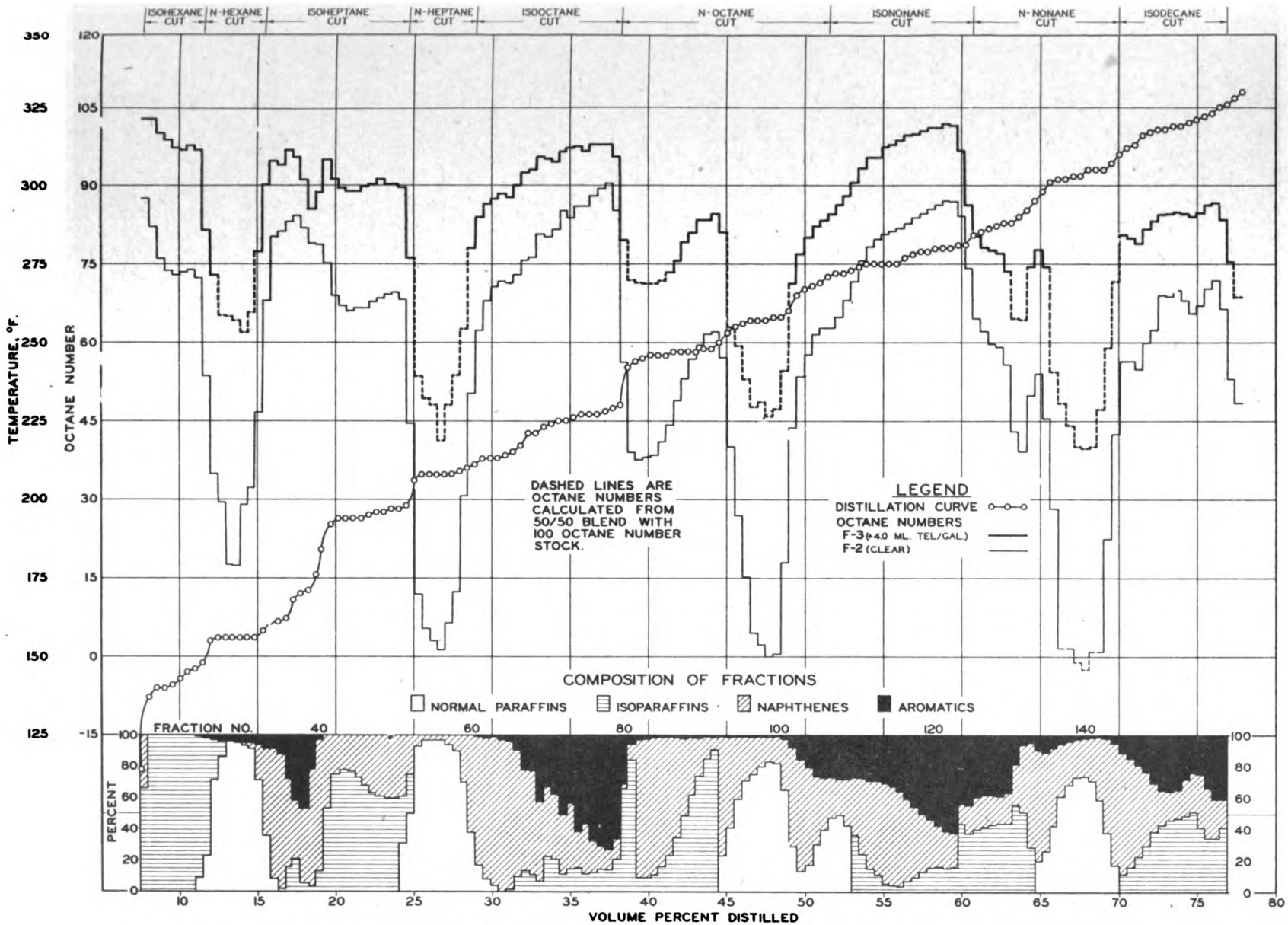

FIGURE II- OCTANE NUMBERS AND COMPOSITION OF FRACTIONS FROM VENEZUELAN NAPHTHA

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routine analyses of crude oil samples. The crude oils analyzed were distributed among the States and Territories, as follows:

Alaska	3	Louisiana	2
Arkansas	1	Michigan	3
California ...	3	New Mexico ...	2
Colorado	4	Ohio	1
Illinois	5	Oklahoma	45
Kansas	3	Texas	17
Kentucky	4	Wyoming	7

The action, instituted a year ago, to obtain samples of crude oils needed to bring the file of analyses to date has been continued. Eighty-six such samples are on hand awaiting analysis.

Relationship of Fuel Composition, Properties, and Performance

Gasoline

Superfractionation studies,[32] which had been carried out by the Bureau of Mines during and after the war, continued to be of interest, and during the current year superfractionation of Santa Barbara, Venezuela, naphtha was completed. Each 0.5 percent fraction in the 100°-326° F. boiling range was analyzed for composition in terms of individual hydrocarbons by the hydrocarbon analysis group method, and its engine ratings by the CFR-F-2 (motor method) and by the CFR-F-3 (aviation lean method) with 4.0 ml. TEL were determined by the fuel-combustion group. In figure 11 the overhead temperature and the octane numbers by both the F-2 and F-3 methods are plotted against sum percent distilled. At the bottom of the chart is a bar-graph that gives the composition of each fraction in terms of paraffins, isoparaffins, naphthenes, and aromatics to indicate relationships between octane numbers and composition. The blending F-2 octane numbers of the individual hydrocarbons were calculated from the octane numbers and composition of the fractions, and the F-3 values were used to improve the accuracy of the values calculated from data obtained on the Oklahoma City naphtha. Some of the data obtained during study of the Santa Barbara naphtha were presented before the Midwest Regional Meeting of the American Chemical Society[33] and submitted to Industrial and Engineering Chemistry for publication.

Continuing such studies, a sample of naphtha from West Edmond, Okla., crude oil has been superfractionated through the same distillation unit, and a study of the properties of the fraction is currently under way.

32/ Ward, C. C., Gooding, R. M., and Eccleston, B. H., Superfractionation Studies, Composition, and Octane Numbers of 0.5 percent Fractions of an Oklahoma City Naphtha: Indus. and Eng. Chem., vol. 39, p. 105, January 1947.

33/ Schwartz, F. G., Gooding, R. M., and Eccleston, B. H., Superfractionation Studies: Naphtha from Santa Barbara, Venezuela Crude Oil: Presented at Regional Meeting of American Chemical Society, Kansas City, Mo., June 23-25, 1947.

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One of the most interesting results from this superfractionation work is the fact that the data on composition, used in conjunction with the data from the engine laboratory where the fuels are tested for their antiknock value according to standard methods, have permitted the calculation of blending octane numbers for individual components of the naphtha. As a result of several studies wherein aviation lean-mixture octane numbers were determined, blending values for hydrocarbons in the range up to normal octane have been fairly well established. Similarly, values for the motor method octane numbers of hydrocarbons are in process of establishment. Information of this type is very useful in estimating the properties of various blends that might be prepared from a given crude oil, and when only a small sample of oil is available it enables the calculations of octane numbers by simply performing a fractionation analysis on a small sample, which provides the necessary data and still leaves the gasoline fractions available for other tests. A summary of the latest data available on blending octane numbers is given in the report on Santa Barbara naphtha.33/

Diesel Fuels

General program. - With the return to peacetime activities throughout the country, there is an unprecedented demand for oils in the boiling range of Diesel fuels. This boiling range includes not only Diesel fuels but also heating oils, jet propulsion fuels, and cracking-charge stock for the manufacture of gasoline, particularly by catalytic processes. Furthermore, a greatly increased demand, particularly for Diesel and heating oils, is forecast. For example, many of the railroads have on order Diesel-electric motive units. Also, the new developments in Diesel engines require a better grade of Diesel fuel than did the older slow-speed engines. All of these factors combined have intensified the demand for good Diesel fuel and at the same time have shown that technical knowledge of the relationship of Diesel-fuel composition and its behavior in an engine is very meager.

Numerous technical organizations dealing with petroleum are cognizant of these facts and have asked the Bureau of Mines to make certain basic studies dealing with the relationships of composition and properties of Diesel fuels. As work of this kind is directly in line with the objective of its chemistry and refining program, the request was welcomed, and a definite program of study of Diesel fuels has been initiated. Along with the Bureau of Mines study of composition, numerous other organizations are making correlated studies of the behavior of Diesel fuels. Thus, in figure 12 are shown some of the cooperative projects on Diesel fuels and their relationships to each other and to the Bureau of Mines program.

At the top of the chart is the Western Petroleum Refiners Association (WPRA) program, concerned with the properties of Diesel fuel as prepared directly from selected crude oils. Proceeding clockwise around the chart, the next topic is the series of studies sponsored by the Coordinating Research Council relating to determination of sulfur limits that technically and economically may be suitable for Diesel fuels. Seven fuels of various characteristics and sulfur content will be studied by numerous cooperators to obtain

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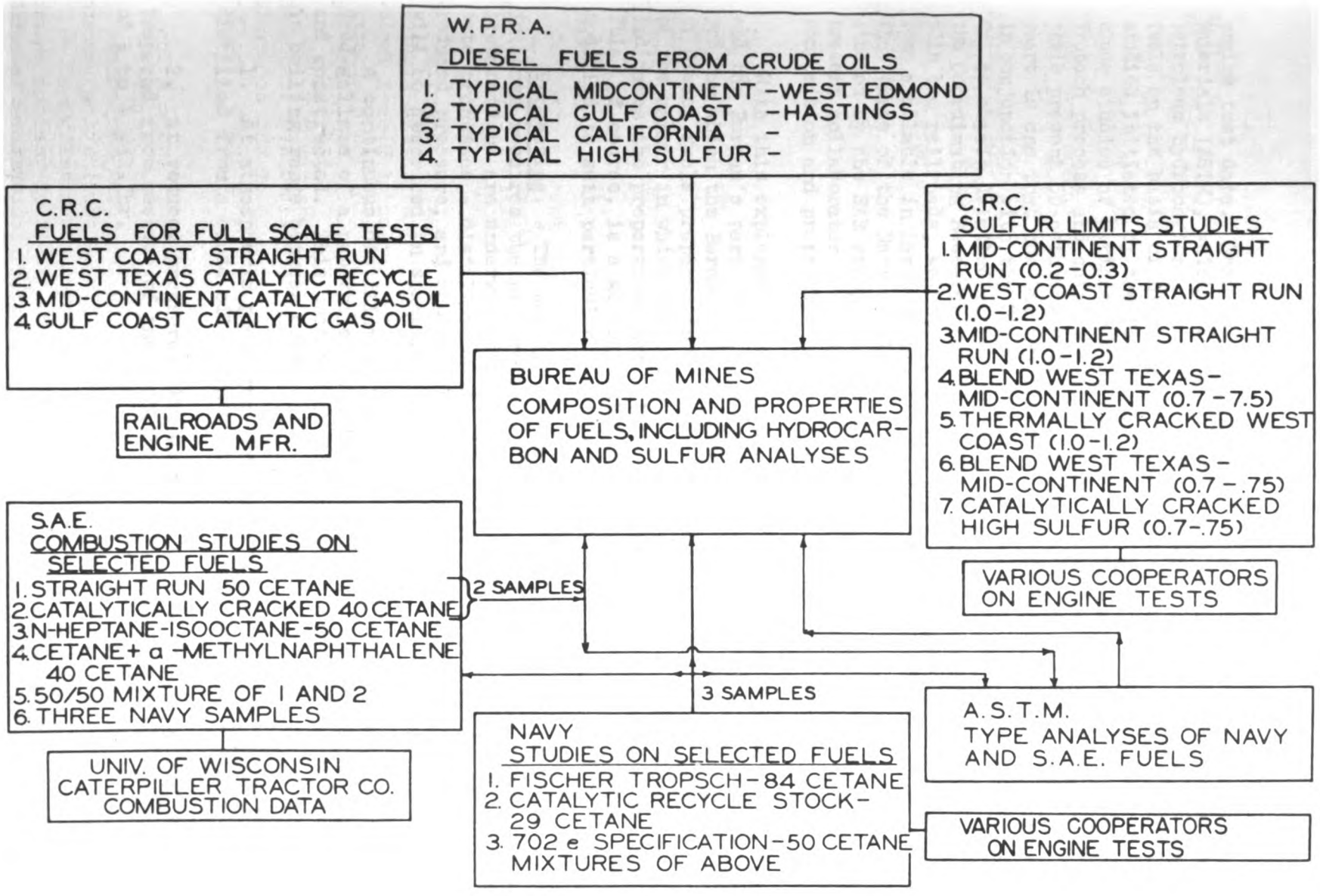
W.P.R.A.
DIESEL FUELS FROM CRUDE OILS
1. TYPICAL MIDCONTINENT -WEST EDMOND
2. TYPICAL GULF COAST -HASTINGS
3. TYPICAL CALIFORNIA -
4. TYPICAL HIGH SULFUR -
C.R.C.
FUELS FOR FULL SCALE TESTS
1. WEST COAST STRAIGHT RUN
2. WEST TEXAS CATALYTIC RECYCLE
3. MID-CONTINENT CATALYTIC GAS OIL
4. GULF COAST CATALYTIC GAS OIL
RAILROADS AND ENGINE MFR.
BUREAU OF MINES
COMPOSITION AND PROPERTIES OF FUELS, INCLUDING HYDROCARBON AND SULFUR ANALYSES
C.R.C.
SULFUR LIMITS STUDIES
1. MID-CONTINENT STRAIGHT RUN (0.2-0.3)
2. WEST COAST STRAIGHT RUN (1.0-1.2)
3. MID-CONTINENT STRAIGHT RUN (1.0-1.2)
4. BLEND WEST TEXAS-MID-CONTINENT (0.7-7.5)
5. THERMALLY CRACKED WEST COAST (1.0-1.2)
6. BLEND WEST TEXAS-MID-CONTINENT (0.7-.75)
7. CATALYTICALLY CRACKED HIGH SULFUR (0.7-.75)
VARIOUS COOPERATORS ON ENGINE TESTS
S.A.E.
COMBUSTION STUDIES ON SELECTED FUELS
1. STRAIGHT RUN 50 CETANE
2. CATALYTICALLY CRACKED 40 CETANE
2 SAMPLES
3. N-HEPTANE-ISOOCTANE-50 CETANE
4. CETANE + a -METHYLNAPHTHALENE 40 CETANE
5. 50/50 MIXTURE OF 1 AND 2
6. THREE NAVY SAMPLES
UNIV. OF WISCONSIN
CATERPILLER TRACTOR CO.
COMBUSTION DATA
3 SAMPLES
NAVY
STUDIES ON SELECTED FUELS
1. FISCHER TROPSCH-84 CETANE
2. CATALYTIC RECYCLE STOCK-29 CETANE
3. 702 e SPECIFICATION-50 CETANE MIXTURES OF ABOVE
A.S.T.M.
TYPE ANALYSES OF NAVY AND S.A.E. FUELS
VARIOUS COOPERATORS ON ENGINE TESTS

Figure 12. - Relationships of cooperative Diesel fuel studies.

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engine test data. Next is the program of the American Society for Testing Materials (ASTM), which, through one of its subcommittees on the analysis of petroleum hydrocarbons, is working out methods for the analysis of Diesel fuels on the basis of hydrocarbon types. At the bottom of the chart are studies initiated by the Navy looking toward future Diesel fuels. They include studies of synthetic oils such as those manufactured by the Fischer-Tropsch process and catalytic recycle stock, as well as mixtures of these and their present 50-cetane specification fuel. The next study indicated on the chart is one that the Society for Automotive Engineers (SAE) is carrying out in conjunction with the University of Wisconsin and the Caterpillar Tractor Co. to obtain detailed combustion data on selected Diesel fuels. Finally, is the Coordinating Research Council (CRC) program for studying, in cooperation with the railroads, selected Diesel fuels of the type that will probably become available in large quantities in the future. It is important to note that three of the Navy samples (those that are not mixtures) also will be studied by the SAE group, the ASTM group, and the Bureau of Mines. The present collaborator with all of these groups, so far as determination of composition and properties is concerned, will be the Bureau of Mines.

With this explanation of the coordinated program of Diesel-fuel study and the Bureau's part in it, now underway, a brief review of the detailed program which the Bureau is following in conjunction with the WPRA on studies of Diesel fuels prepared from crude oils is in order. Table 3 is an outline of the manner in which the crude oil is processed into small fractions and indicates the properties that will be determined on the various fractions. This, of course, is a general outline and, as the studies progress, may be modified to suit particular conditions that may arise.

Processing. - The Western Petroleum Refiners Association program referred to above requires the preparation of Diesel fuels from crude oils. Such preparations are underway currently at the Bureau and consist of three separate processes - distillations in a continuous still, superfractionations at reduced pressure, and separations by silica gel. Each of these processes will be described in somewhat more detail below.

A continuous distillation unit that could be used to prepare several hundred gallons of a naphtha or gas oil directly from the crude oil was designed and constructed. This unit was so designed that there would be little overlap in boiling range between consecutive cuts produced by the following conditions:

1. At atmospheric pressure: Preparing a 350°-400° F. end-point naphtha distilled from a crude oil charged at a feed rate of 5 to 6 gal/hr.

2. At reduced pressure: Preparing a 700°-750° F. end-point gas oil prepared from residue of the atmospheric distillation charged at a feed rate of 3 to 4 gal./hr.

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TABLE 3. - Outline of crude-oil studies: Objective - Diesel fuels

Crude oil (400 gallons)
Top in continuous
still to 350° F.

Gasoline
(Reserve for
other studies)

Topped crude oil (300 gallons)
Vacuum flash in continuous
still to give a 650°-700° F.
end point product

Diesel fuel (100 gallons)
Vacuum fractionate
taking cuts of 2,000 cc.
(approx. 0.53 percent of
Diesel fuel, 0.13 percent of crude oil)

Residuum (save)

190 fractions of 2,000 cc. each
Divide into two parts
one of 1,200 and one of 800 cc.

Determine the properties listed below, as indicated by "X", where volume of sample and other conditions permit

Filter 1,200 cc.
through silica gel

	Paraffin-naphthene fractions	Aromatic-sulfur fractions	800 cc. of original fraction
Volume percent aromatics		X	X
Volume percent paraffins-naphthenes	X		X
Cetane number	X	X (by blending)	X
Refractive index (D, g, e lines)	X	X	X
Density, 20° F.	X	X	X
Aniline point	X		X
Viscosity, 20° C. and 37.8° C.	X	X	X
Carbon-hydrogen ratio	X	X	
Infrared spectra	X	X	X
Ultraviolet spectra		X	X
Sulfur content (if any)	X	X	X
Freezing point (to -100° F.)	X	X	X
Flash point, °F.	X	X	X
Molecular weights	X	X	X
Nitrogen content (California)		X	X
Weight percent naphthene rings	X		X
Weight percent aromatic rings		X	X
Weight percent paraffins plus paraffin side chains	X		X
Volume percent paraffins and volume percent mono- and dicyclic naphthenes	X		X

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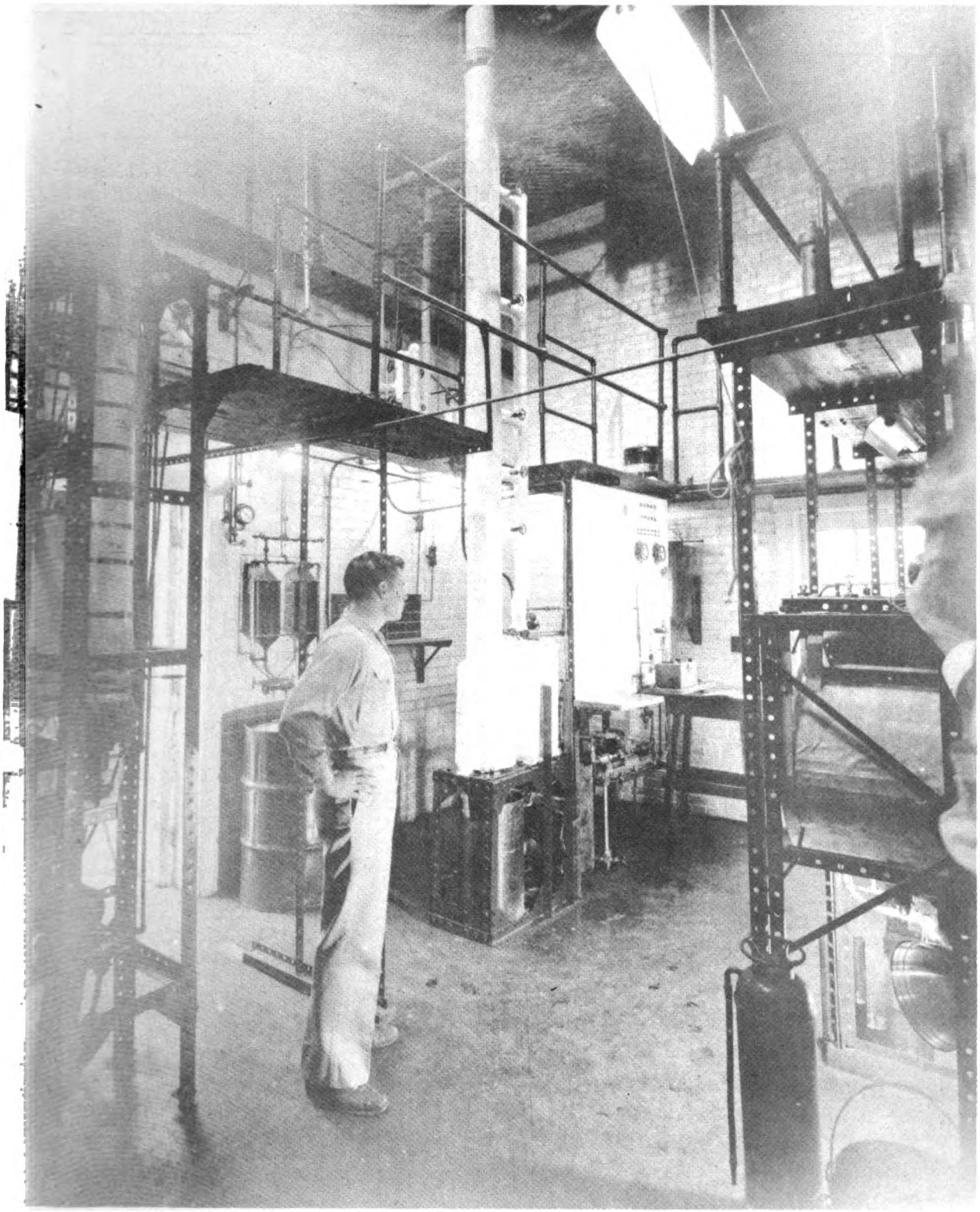

gure 13. - Continuous distillation unit used in the preparation of gasoline and Diesel fuel fractions.

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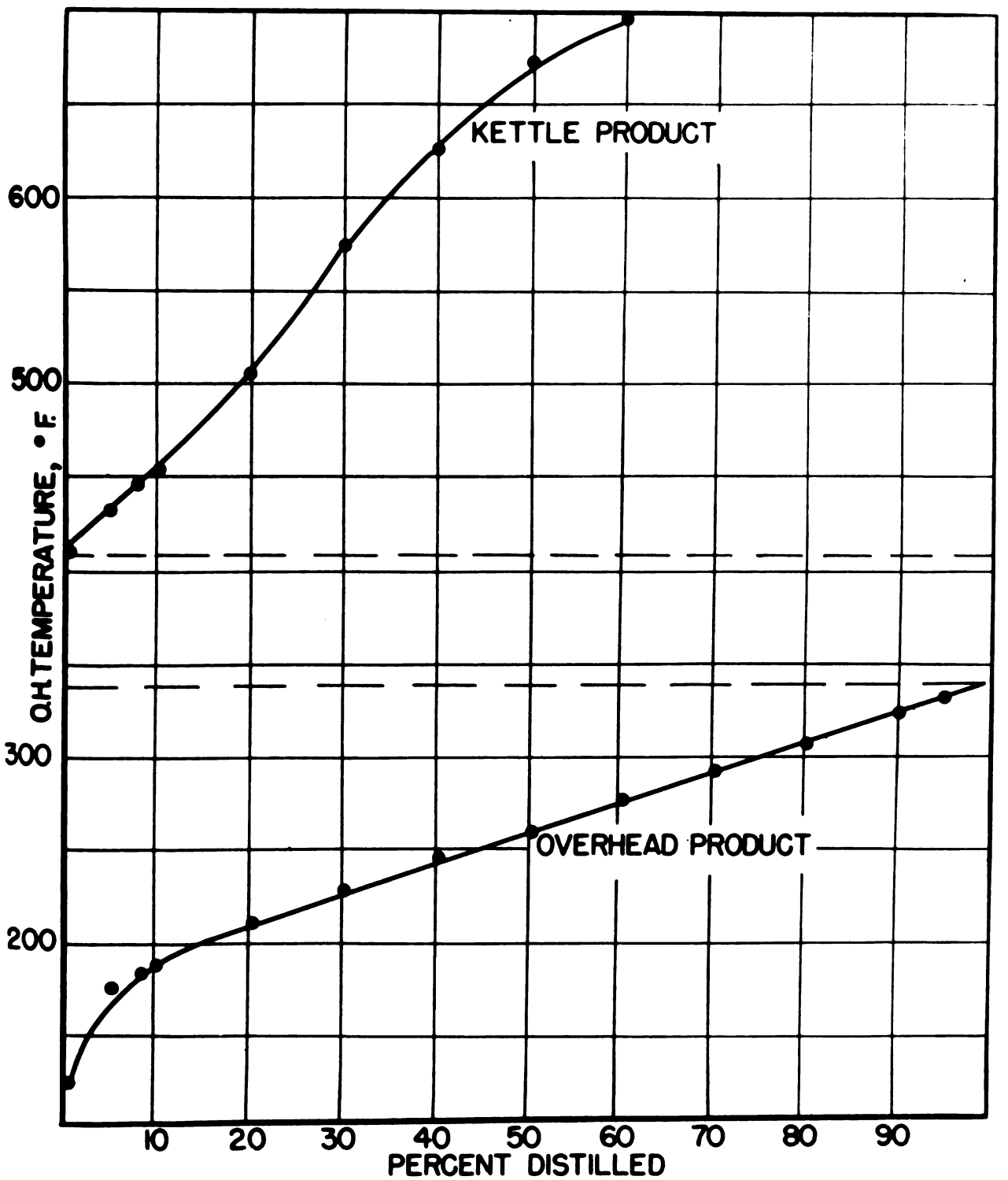

Figure 14. - Distillation curves on products from continuous still at atmospheric pressure.

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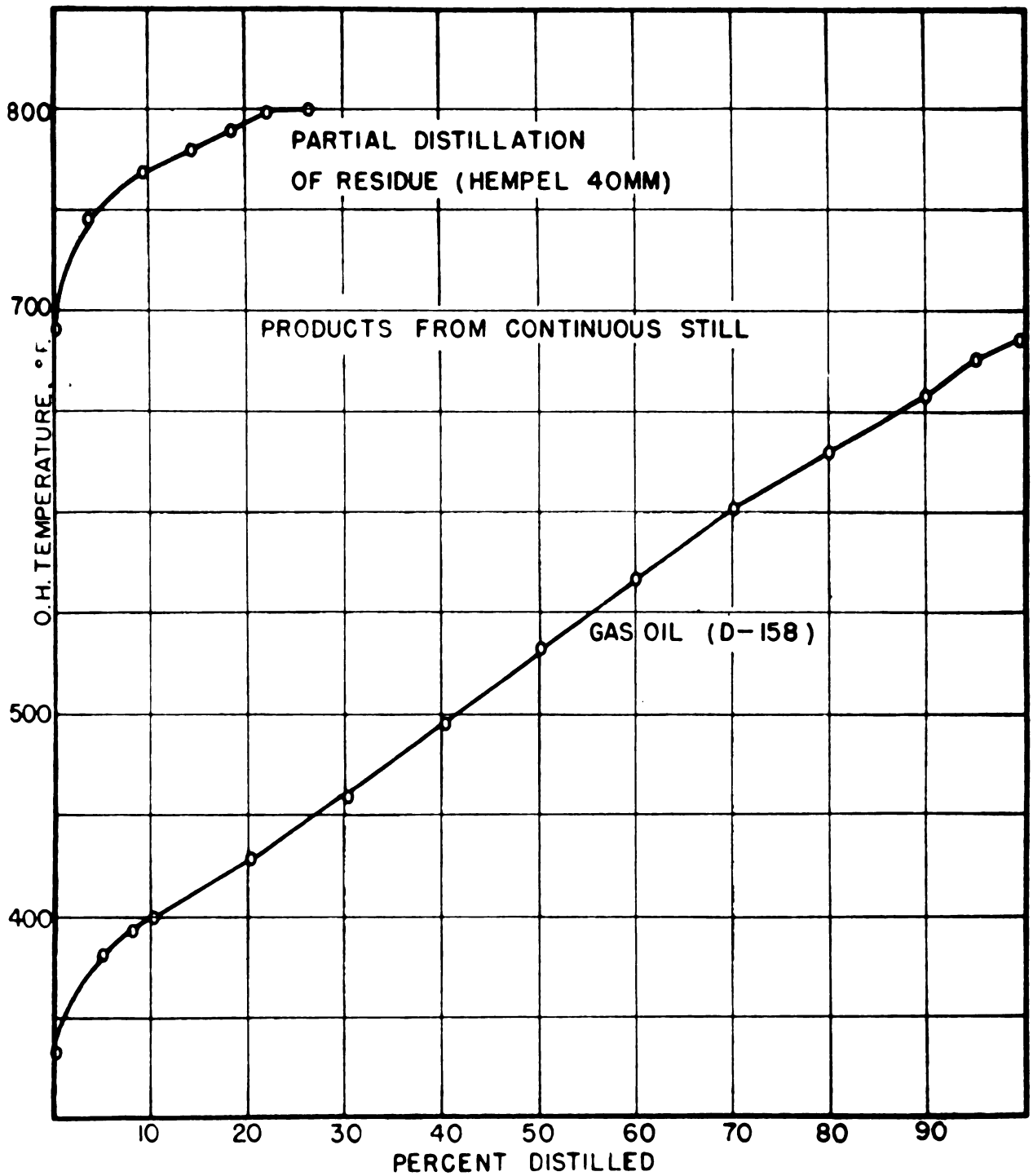

Figure 15. - Distillation curves on products from continuous still at reduced pressure.

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The unit is shown in figure 13, and typical conditions during operation are given in table 4.

TABLE 4. - Continuous distillation unit operation conditions

	Atmospheric	Vacuum
System pressure, mm. Hg.	745	10
Feed rate, gal./hr.	6.2	3.7
Top temperature, °F.	260	375
Reboiler temperature, °F.	580	615
Feed temperature, °F.	635	640
Flash temperature, °F.	420	570
Differential pressure, mm. Hg.	64	43
Overhead, volume percent of charge	33	65

Laboratory distillation curves on overhead and bottoms products made during trial runs at atmospheric pressure and at 10 mm. of mercury pressure, absolute, are shown in figures 14 and 15, respectively. Figure 14 shows a gap of about 70° F. between the end-point of the overhead product and the initial boiling point of the bottoms. Figure 15, which gives curves for a gas-oil cut and the corresponding bottoms product, indicates little gap. However, these curves are not strictly comparable, as the laboratory distillation on the gas oil was made at atmospheric pressure, and the bottoms-product curve is from a Hempel distillation at 40 mm. pressure with the temperatures corrected to atmospheric pressure.

A paper describing this continuous distillation unit was presented at the Midwest Regional Meeting of the American Chemical Society,[34] and this paper has been submitted to Industrial and Engineering Chemistry for publication.

A 550-gallon sample of West Edmond, Okla., crude oil was processed through the continuous distillation unit at atmospheric pressure to prepare 174 gallons of 96°-376° F. boiling-range naphtha for superfractionation studies. A 264-gallon sample of the bottoms product was processed through the unit at 10 mm. pressure to prepare 172 gallons of 744° F. end-point gas oil for superfractionation at reduced pressure.

An aliquot portion of the gas oil cut from West Edmond crude oil was added to the residue of the naphtha superfractionation and the fractionation continued to 400° F. at atmospheric pressure. Then pressure was reduced to 50 mm. and then to 20 mm. of mercury pressure, and distillation was continued until an overhead product was obtained that had a boiling point corresponding to 637° F. at atmospheric pressure. One-half percent fractions were collected throughout this range for silica gel adsorption treatment and property determinations as shown in table 3. Most of the original fractions have been rated

34/ Ward, C. C., and Schwartz, F. G., Construction and Operation of a Pilot Size Continuous Distillation Unit: Presented at Regional Meeting of American Chemical Society, Kansas City, Mo., June 23-25, 1947.

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in terms of cetane number, and the majority of their properties have been determined. About 40 fractions have been filtered through silica gel, and some properties on the paraffin-naphthene and aromatic portions have been determined.

A 40-gallon batch still was modified to operate at 5 mm. pressure, and experimental runs are being made with it to obtain data with which to design a 100-gallon batch vacuum superfractionation unit.

Since 1945, silica gel has been used by the Bureau as a means of separating paraffins, naphthenes, and aromatics from petroleum products. This method is being used extensively in the current studies of Diesel fuels. Silica gel adsorption has been used effectively for separating the aromatic type hydrocarbons from the paraffin-naphthene types, and two additional pilot-scale silica-gel adsorption columns were constructed to take care of the large number of samples that are being processed in this manner. One column 3 inches in diameter and 21 feet long is similar to the previous column, except that it has three 500-watt heating sections instead of two, so as to provide more heat during regeneration. A column 1-1/2 inches by 21 feet long was constructed to rerun intermediate fractions from the larger columns and for use when running smaller size fractions.

Each of the 3-inch columns has a capacity of 38 pounds of silica gel, which is either discarded or regenerated after each run. Several different schemes of regeneration have been tried, but the following procedure appears to be the most satisfactory. Steam at 35 psi. is admitted to the top of the column for 10 to 12 hours while the column temperature is maintained above the steam-condensation temperature. The steam is then cut off, and air is passed through the column for about 35 hours while the column temperature is kept at 350° to 450° F.

The activity of the reactivated gel is checked by comparing the volume of aromatics adsorbed from a standard solution by 50 grams of gel, as compared with the volume adsorbed by 50 grams of unused gel.

The columns described above are used in certain parts of the Diesel-fuel studies. For example, the oils furnished by the Society of Automotive Engineers are being filtered through silica gel prior to distillation. On the other hand, in the schematic program shown in table 3, many fractions of relatively small volume have to be separated by means of silica gel. For this purpose, a smaller type of column is used, and one of the more recent designs is shown in figure 16. In the study of these Diesel-fuel fractions, a battery of about 15 columns of various types is in constant use (fig. 17). For the higher-boiling ranges, pressure must be applied to force the sample through the fine gel; consequently, the newer columns are constructed of stainless steel or copper and can be used at pressures up to 300 pounds per square inch.

Composition and properties of Diesel fuels. - One of the first crude oils studied was from the Dupo, Ill., field. This is a small field in southwestern Illinois producing a rather unusual crude oil, which yields an exceedingly high cetane-number fuel. This oil was studied primarily as an orientation problem, but some interesting facts were obtained.

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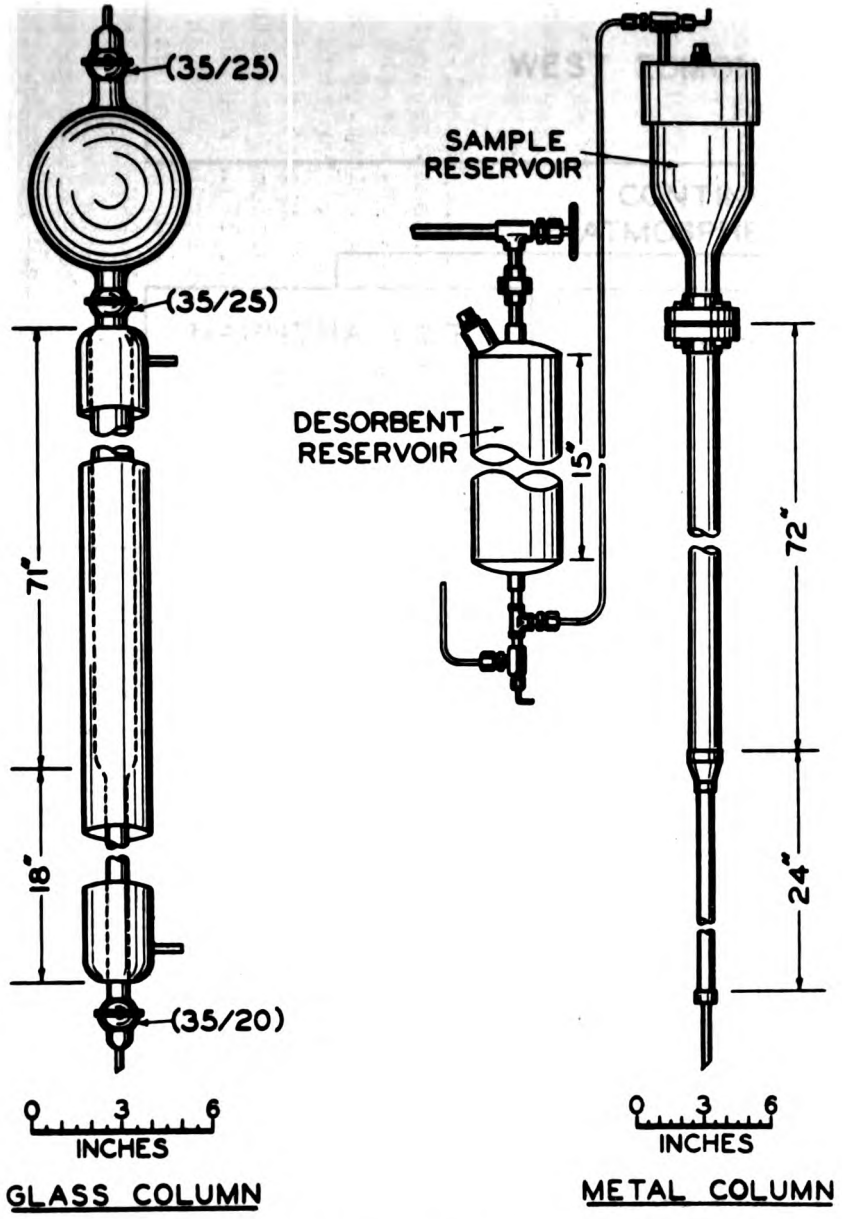

Figure 16. - Adsorption columns.

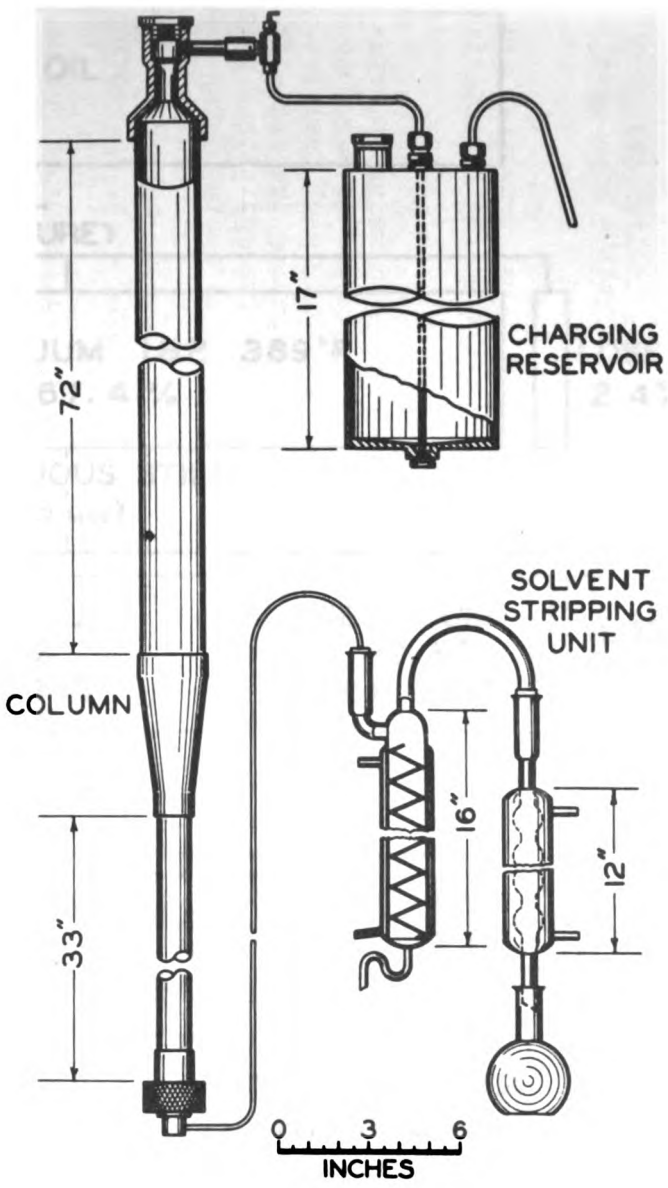

Figure 17. - Metal adsorption column.

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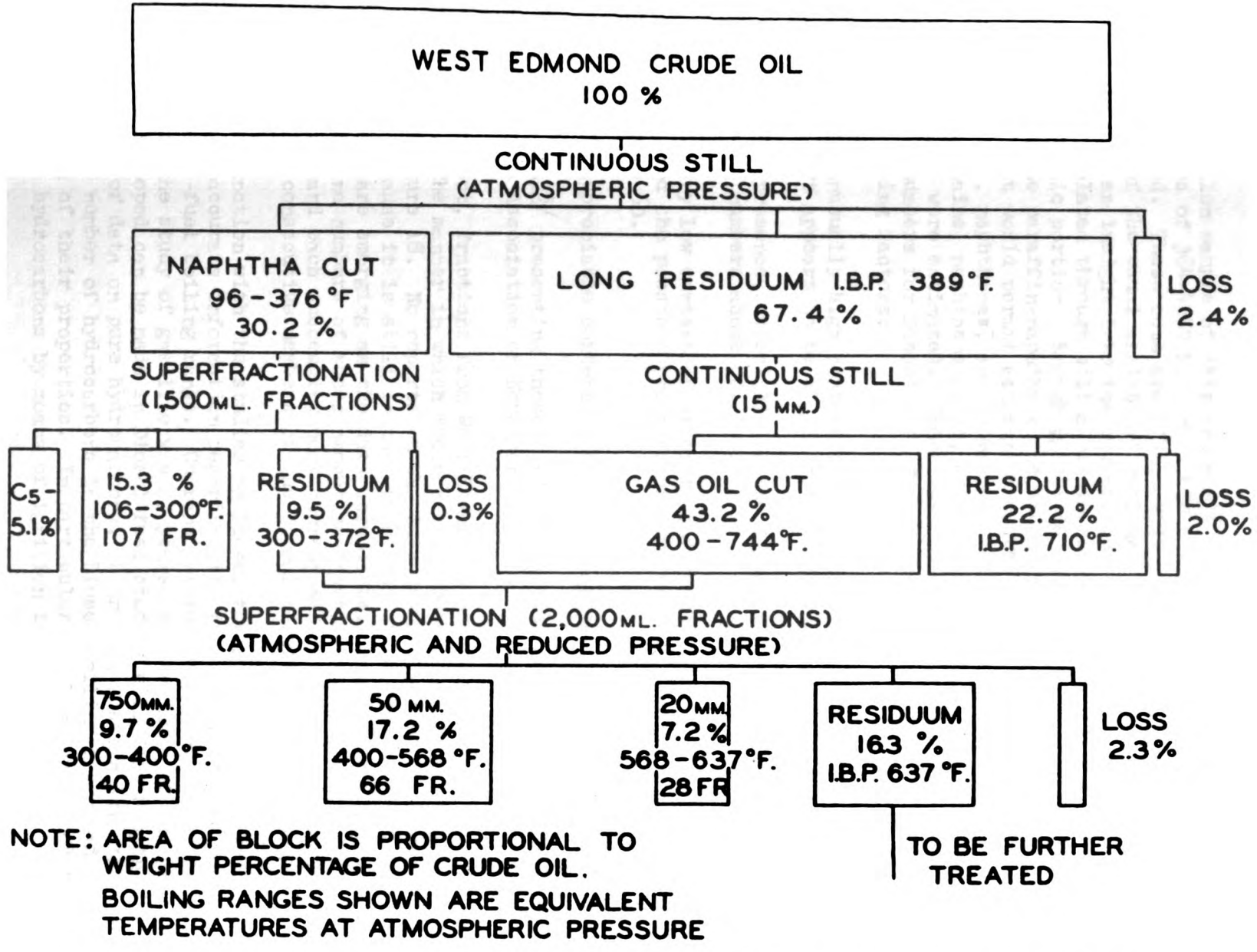

Figure 18. - Schematic chart of processing the West Edmond crude oil to produce Diesel fuel.

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A 40-gallon sample of this crude oil was distilled, and three cuts having boiling ranges of 364-458° F., 482°-542° F., and 582°-650° F., respectively, were collected. These cuts are of too wide a boiling range for successful application of the usual analytical methods. Nevertheless, an attempt was made to gain an insight into the composition of the cuts. A portion of each cut was percolated through silica gel to separate it into a paraffin-naphthene and an aromatic portion. Enough properties were determined on each original cut and on the paraffin-naphthene and aromatic portions from each cut to provide data that would permit estimation of the composition in terms of paraffins, olefins, naphthenes, and aromatics. Percentages of paraffins plus paraffin side chains, naphthene rings, aromatic rings, and aromatic rings per molecule also were estimated. These data lead to the conclusion that the high cetane numbers for Diesel fuel from Dupo crude oil are due to the following contributing factors:

1. An unusually high content of paraffin hydrocarbons, of which a considerable part appears to be of the normal structure.

2. The presence, especially in the higher boiling portion, of naphthenes having cetane numbers above 60.

3. A very low content of aromatic compounds, especially of dicyclic aromatics, and the possible presence of alkylated benzenes having cetane numbers above 60.

4. No appreciable content of dicyclic naphthenes.

A report[35/] presenting these findings was submitted to the Western Petroleum Refiners Association on November 1, 1946.

At present, fractions from West Edmond crude oil are being studied intensively. The manner in which these samples have been prepared is illustrated in figure 18. No reports on the data resulting from this work have been prepared, because it is still in the unfinished stage; but a number of interesting facts are emerging as the data accumulate. One fact of importance is that the cetane numbers of the consecutive fractions form a series of peaks and valleys, and each succeeding peak corresponds to the occurrence in those fractions of consecutive members of the normal paraffin hydrocarbon series.

In conjunction with the studies on Diesel fuels, it is exceedingly important to have accurate information regarding the properties of pure hydrocarbons in the Diesel-fuel boiling range. Current information along these lines is about where the study of gasoline was 25 years ago, and much of the progress which it is hoped can be made in Diesel-fuel studies will depend upon the availability of data on pure hydrocarbons. Petrov, a Russian scientist, has synthesized a number of hydrocarbons in the Diesel boiling range and determined certain of their properties. In particular, he has determined the cetane number of the hydrocarbons by means of ignition in a bomb, and it is claimed

35/ Progress Report No. 1: The Composition and Properties of Diesel Fuels. Nov. 1, 1946.

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that these data correlate almost exactly with data obtained by means of a standard test engine. In order to have available all the information that has been published regarding pure hydrocarbons in this boiling range, the Bureau prepared a report compiling all of these data and presented it at the Regional Meeting of the American Chemical Society at Kansas City in June.36/ The tables in this report present all the available data on pure hydrocarbons so far as cetane numbers, either determined or estimated, are concerned.

As mentioned, much of the Russian work has been done with a bomb, but only a few correlations between the bomb and tests on a standard engine are available. However, those few are sufficiently good to make it desirable to have more complete substantiation of the bomb method. To make full use of the work in the literature, it becomes necessary to validate the use of the bomb for this purpose, and the Bureau is developing a bomb procedure similar to that used by the Russian investigators to determine the ignition lag. This bomb will have the additional advantage that, if successful, it will use only a very small sample, and many other pure hydrocarbons which have been synthesized in this country, such as those made by API project No. 42 at Pennsylvania State College, can be tested.

Utilization of Petroleum Products

Among the most important contributions to many of the reports thus far referred to are the engine ratings of the gasoline and Diesel-fuel fractions. As one of the objectives of this research work is to delineate the relationships of fuel characteristics as determined by chemical and physical tests with their behavior when burned in an engine, it is apparent that a well-equipped engine laboratory with competent operating personnel is necessary to any research work on fuels.

During the year, the engine laboratory at the Bartlesville Petroleum Experiment Station has supplemented its equipment by (1) the conversion of one of its test units from the aviation lean-mixture method to the ignition-delay method for rating ignition quality of Diesel fuels and their components in terms of cetane number method; (2) acquisition by loan from the Army of a 4-speed supercharge engine for rating aviation fuels; and (3) loan from the Cooperating Fuel Research Committee of a test unit for rating motor fuels by the motor method.

The Diesel test unit was put in operation in September, and the latter two units were being installed at the end of the year.

With these additions, the engine laboratory will have five test engines one motor-method unit, one aviation lean-mixture method unit, two aviation supercharge units, and one cetane-method unit.

The Diesel test unit consists of a continuously variable-compression single-cylinder engine belted to an electric motor, which serves to absorb

36/ Caudle, B. H., and Puckett, A. D., Cetane Number of Hydrocarbons: Presented at Regional Meeting of American Chemical Society at Kansas City, Mo., June 23-25, 1947.

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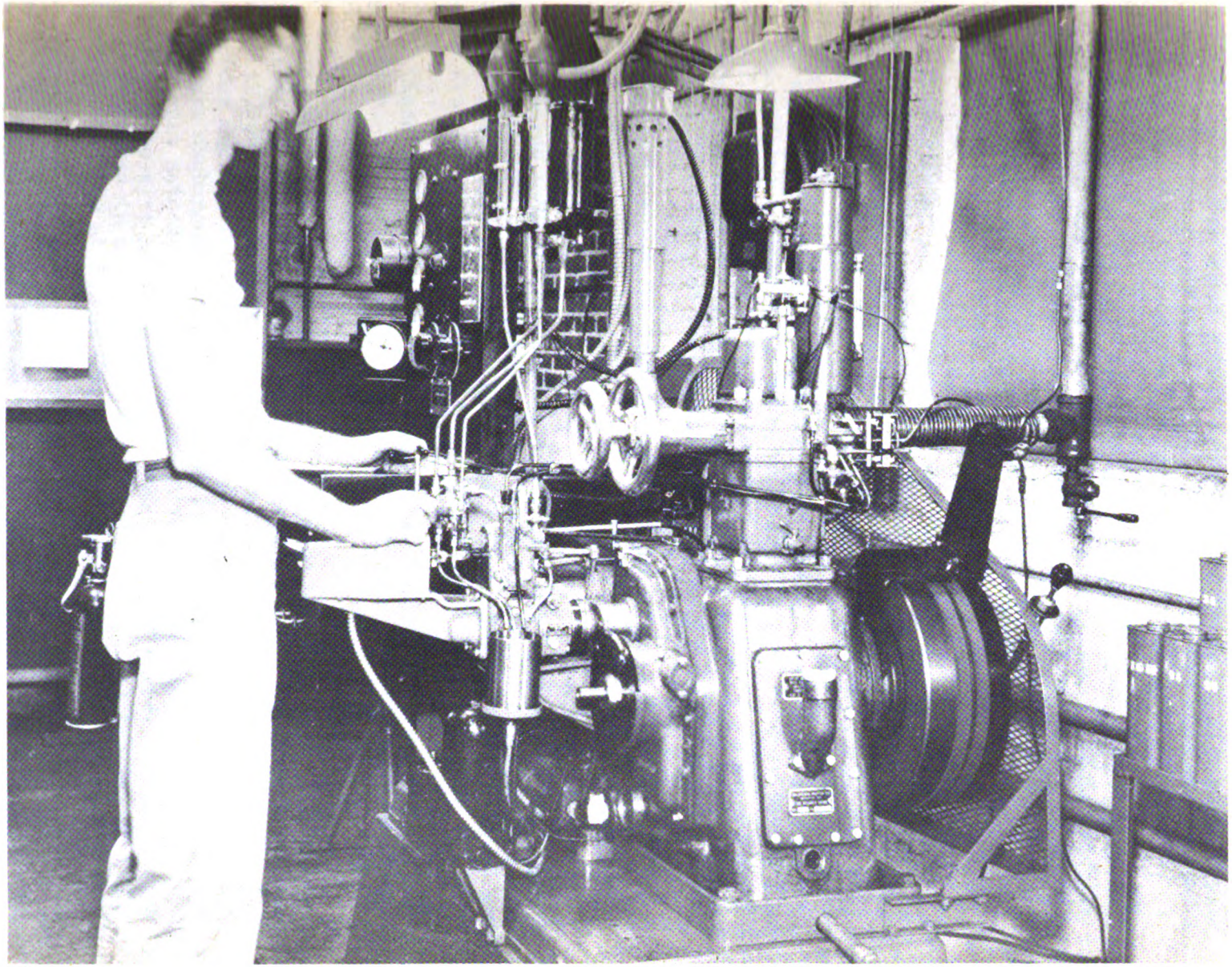

Figure 19. - Photograph of test engine used for determining cetane number of Diesel fuels.

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the power generated by the engine and also controls its speed. The engine operates on the conventional Diesel cycle, the fuel being injected into a combustion chamber whose volume can be varied by means of a movable plug, thus varying the compression ratio. The instant that fuel is injected and the time that ignition occurs are indicated by instruments.

When fuel is injected into the combustion chamber, ignition occurs after an interval of time which is known as ignition delay. If this delay is relatively large, the accumulated fuel burns with great rapidity, resulting in rough operation or knock. A short ignition delay, on the other hand, results in easier starting and smoother operation of the engine. These are desirable characteristics of a Diesel fuel.

Normal cetane, a hydrocarbon that has a very short ignition delay, has been chosen as the reference fuel for comparing the ignition quality of Diesel fuels and has been chosen arbitrarily as 100 on the ignition-quality scale, and alpha methylnaphthalene, a hydrocarbon that has extremely long ignition delay, has been chosen as zero on that scale. Blends of these two reference fuels are used to make up the body of the cetane scale from zero to 100. The ignition delay of test fuels is matched or bracketed between blends of reference fuels of known ignition quality and ratings expressed in cetane number. For economic reasons, calibrated secondary reference fuels available from Shell Oil Co., Inc., at lower cost are used in all normal testing.

Figure 19 shows the Diesel test unit in operation.

Gasoline

A large part of the testing on gasoline has been on samples prepared by other groups of the Chemistry and Refining Section, and consequently the engine laboratory has been called upon to rate samples prepared from crude oils from Santa Barbara, Venezuela, and West Edmond, Okla.

These ratings have involved all three methods of tests commonly used on gasoline, i.e., aviation lean-mixture, aviation supercharge or rich mixture, and the ASTM motor method.

In addition to work on samples prepared by the research laboratory are tests of fuels submitted by the Exchange Group of the Coordinating Research Council, recently transferred to the jurisdiction of Committee D-2 of the American Society for Testing Materials. Samples of both aviation and motor fuels are exchanged on a national and local basis, and these tests form one of the best methods of enabling the operators to keep their engines in correct condition to give accurate results. The value of these exchange groups has been discussed in a paper[37] presented at the Regional Meeting of the American Chemical Society at Kansas City. These local operation and maintenance groups,

37/ Wade, G., and Eccleston, B. H., Improving the Reproducibility of Anti-Knock Ratings of Aviation Fuels: Local CFR Operation and Maintenance Groups: Presented at Regional Meeting of American Chemical Society, Kansas City, Mo., June 23-25, 1947.

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which are an outgrowth of war activities, have been continued in the post-war period, and the Tulsa-Bartlesville Group, of which one of the Bureau of Mines staff is leader, is carrying on much needed cooperative testing to iron out difficulties that arise in the test procedure.

Another aspect of gasoline utilization is related to the various inspection tests that determine the quality of the gasoline produced. The American Society for Testing Materials is the foremost organization interested in this work, and several representatives of the Bureau of Mines are members of the Committee D-2 of ASTM, which deals with petroleum products, and are also members of subcommittees related to specific tests for gasoline. Thus, during the current year cooperative work has been carried out by the Bureau of Mines on determination of sulfur in gasoline, determination of tetraethyl lead in gasoline, determination of vapor pressure, methods of hydrocarbon type analyses for gasolines, and determination of aniline points. In addition, one of the staff is the national leader of the Motor Fuels Exchange Group, whose functions have been discussed above.

Another study bearing directly upon utilization by the consumer is the national motor gasoline surveys. These surveys are made in cooperation with the Coordinating Fuel Research Committee of the Coordinating Research Council, Inc., and have been conducted since 1936, with the exception of 1942, when two of the reports were omitted. Two surveys were completed during the fiscal year 1947. The report for the summer of 1946 was published in December 1946,38/ and compilations for the survey of winter 1946-47 were completed by June 1, and the report appeared in August 1947.39/

Both surveys reflect the shortage of tetraethyl lead, in that the average octane values of motor gasolines were lower than those reported in the survey for the winter 1945-46, when the highest octane numbers for premium and regular-price motor fuels in the survey's history were recorded. The octane ratings were well above those of the summer of 1945, however, when wartime restrictions were in effect. Following are the national average motor-method octane ratings of premium-price and regular-price gasolines for the two surveys made during the fiscal year 1947 and, for comparison, of the two surveys in the preceding year:

	Fiscal year 1946		Fiscal year 1947	
Grade of gasoline	Summer 1945	Winter 1945-46	Summer 1946	Winter 1946-47
Premium price.....	74.9	80.9	78.3	78.5
Regular price	69.7	75.9	74.4	75.0

The reports also give data on gravity, sulfur content, Reid vapor pressure research octane number, and distillation analysis. In addition, the report of winter 1946-47 shows values on corrosion, gum, and T.E.L. (tetraethyl lead) for the first time in the survey series.

38/ Blade, O. C., National Motor-Gasoline Survey, Summer 1946: Bureau of Mines Rept. of Investigations 4063, 1946, 37 pp., 3 figs.
39/ Blade, O. C., National Motor-Gasoline Survey, Winter 1946-47: Bureau of Mines Rept. of Investigations 4146, 1947, 38 pp., 3 figs.

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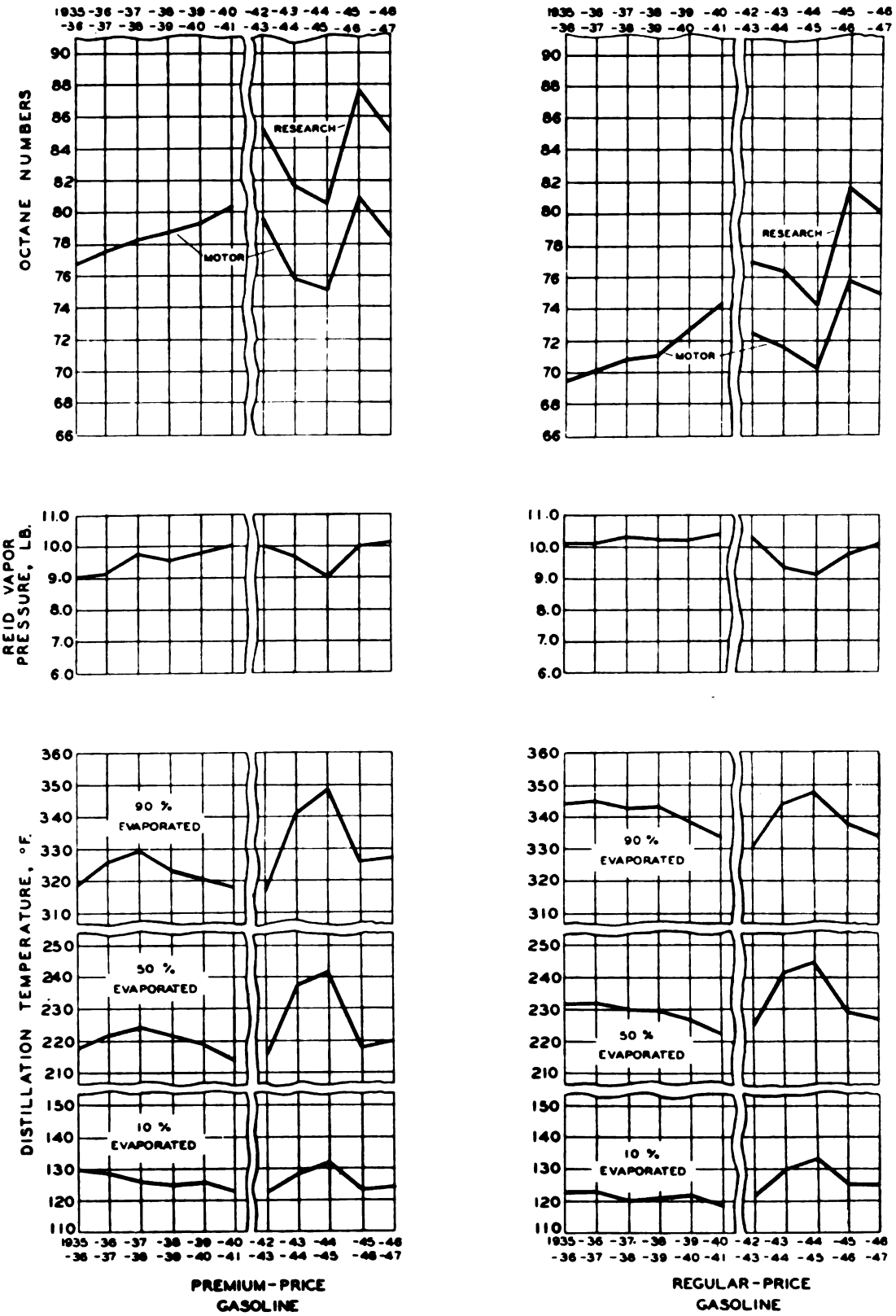

Figure 20. - Comparison of gasoline characteristics from winter surveys of 1935-36 through 1946-47. No plots are shown for the winter of 1941-42 as the surveys were discontinued during 1942.

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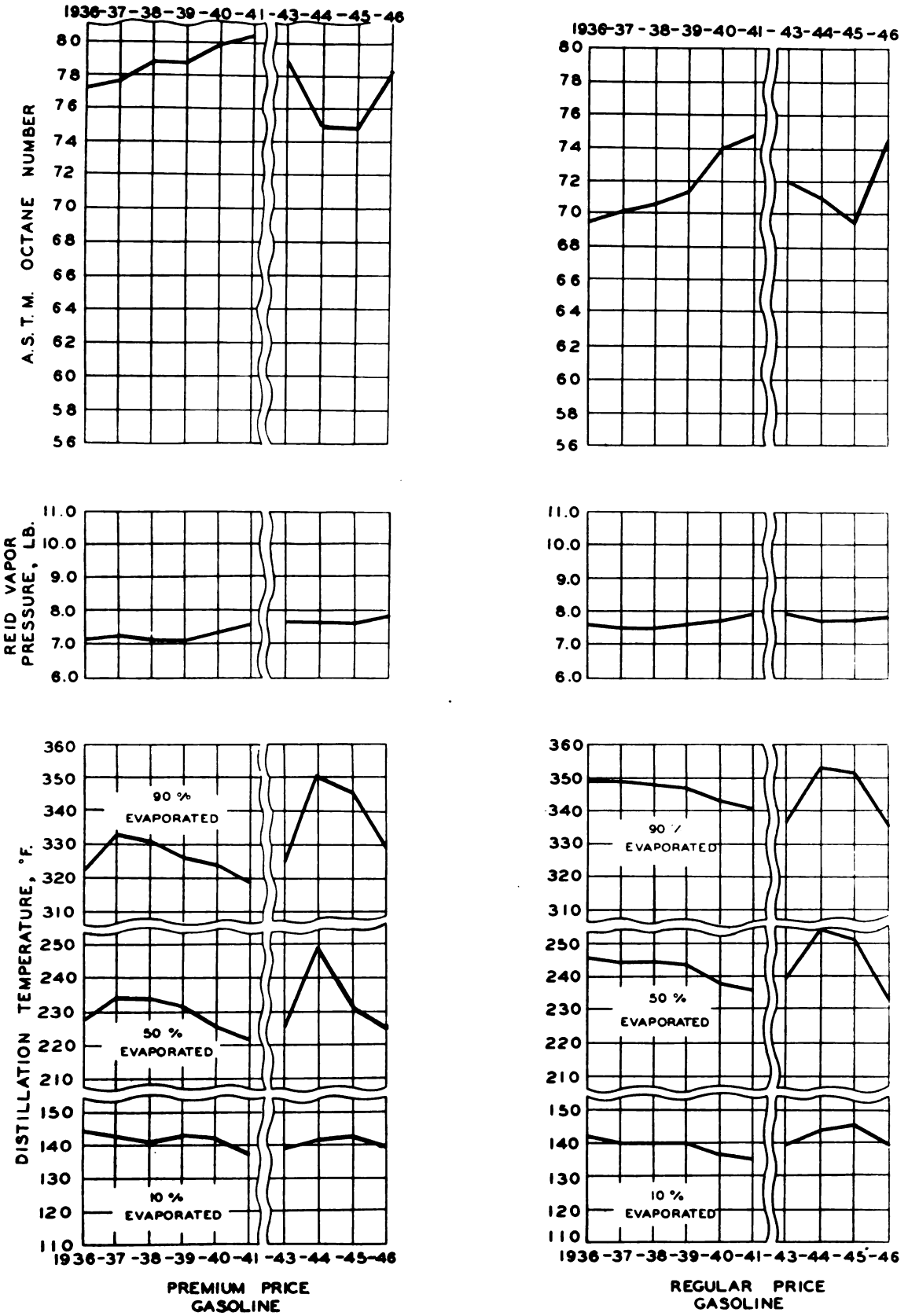

Figure 21. - Comparison of gasoline characteristics from summer surveys of 1936 through 1946. No plots are shown for the summer of 1942, as the surveys were discontinued during 1942.

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Figures 20 and 21 from the last survey report show the trend of octane numbers, vapor pressure, and three distillation-temperature points for the two grades of motor fuel during the winters and summers, respectively.

Samples of gasoline represented in the surveys are collected from service stations by commercial organizations (oil and motor companies) and tested in their laboratories, and the results are transmitted to the Bureau of Mines for compilation. For the summer 1946 report, 3,011 samples were obtained by 17 contributing organizations from 233 cities in 40 States and the District of Columbia and represent the products of 113 marketers of gasoline. For the winter 1946-47 survey, 4,544 samples were collected by 20 contributing companies from 282 cities in 40 States and the District of Columbia and represent the products of 124 marketers of motor fuel.

Recent survey reports include a map of the United States that shows the distribution and numbers of the samples collected for the gasoline survey. Inspection of the maps shows good representation in most parts of the country.

For the past several years the Coordinating Research Council has also conducted, in cooperation with the National Bureau of Standards, surveys of aviation gasoline. Recently, because of changes in personnel and policy in the National Bureau of Standards, this survey has been transferred to the Bureau of Mines and is being conducted at the Petroleum Experiment Station at Bartlesville, Okla. It continues as a cooperative project with the Coordinating Research Council and is conducted particularly to provide information of value to the aviation industry with regard to vapor lock studies. Previously, the results of these surveys had not been reported, except to certain interested committees, but under the new arrangement these surveys will be published in a manner analogous to the method used for the motor-gasoline surveys.

The primary objectives of this survey are to ascertain with considerable accuracy the vapor pressure, distillation range, density and viscosity of aviation gasolines in current production in the United States. Initiation of this work has required the installation of considerable special apparatus - for example, a special vapor-pressure apparatus for measuring vapor pressure to a precision of 0.02 psi, and viscometers of greater precision (Fenske Master Viscometers) than ordinarily used in petroleum testing. This program has undergone many delays, but the first semiannual report covering spring 1947 production of aviation gasoline probably will be published early in 1948. This will include not only original data obtained at the Bureau laboratories but also data on the samples furnished by the cooperating companies. Samples for the second survey are being received. Because of more familiarity with the program, the second survey should not require as much time as the first.

Diesel Fuels

As in the study of gasoline fractions, engine testing is one of the most important phases of the current studies relating to Diesel fuels. Thus, during the current year cetane-number determinations have been made on fractions prepared from crude oils from Santa Barbara, Venezuela; West Edmond, Okla.; Dupo, Ill.; and Slaughter, Tex.

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The Diesel program outlined earlier in this report indicates that the many small fractions of Diesel fuels and their subsequent separation by silica gel will require the determination of a great many cetane numbers in the course of this program. For example, on the West Edmond work currently underway, 124 determinations have been made already; but the West Edmond work, when finished, will probably require between three and four hundred determinations.

As with gasoline testing, the operators are kept informed as to the condition of their engine by monthly exchange samples on a national basis. Also, in connection with the Diesel fuel program, determinations of the cetane ratings of pure hydrocarbons and blends of pure hydrocarbons help form a background of information upon which the research data from the crude-oil studies may be based.

There are also ASTM cooperative tests applicable to Diesel fuels. Of particular importance during the past year has been the development of methods suitable for hydrocarbon type analysis of Diesel fuels. Also, the application of sulfur-determination methods and aniline point methods to the Diesel fuel range have been carried out.

Miscellaneous

Another ASTM cooperative study, which is applicable not only to Diesel fuels but to all petroleum products that crack upon distillation at atmospheric pressure, is the development of a standardized reduced-pressure distillation method for evaluating such products. The Bureau is cooperating actively in this development because such a test is of considerable interest in relation to its crude-oil studies.

Another aspect of utilization in which the Bureau has been interested for a number of years but has not carried out experimental work for some time is the utilization of natural gas for chemical products. In 1930, the Bureau published an information circular on this subject. This proved to be a popular publication. It was revised in 1940 and again in 1947.40/ The increase in importance of this subject has been exceedingly great and is illustrated in a general way by the growth in size of the publication from 5 to 24 pages in 17 years. Charts in the latest revision show products that can be obtained from natural gas by decomposition, oxidation, halogenation, nitration, and sulfurization. In addition, some of the relationships between the various conversion processes used in the petroleum industry are described, and a bibliography of 218 references is given.

Analytical Methods

Modern analytical methods are based more and more upon special instruments, and in hydrocarbon analyses properties of pure hydrocarbons are equally important.

40/ Smith, H. M., and Hollinman, W. C., Utilization of Natural Gas for Chemical Products: Bureau of Mines Inf. Circ. 7347, March 1947, 24 pp., 12 figs.

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Instrumentation

In any investigation to determine the value of a petroleum product as a fuel or raw material, the physical properties are of primary interest. The properties of principal interest are density, viscosity, and refractive index, to which may be added some type of distillation or boiling-point characteristic. These properties are not only basic but, fortunately, are relatively easy to obtain. The information supplied by these properties is augmented by that supplied by data such as freezing points, ultraviolet and infrared absorption analyses, silica-gel adsorption analyses, and others obtained with greater difficulty.

Viscosity usually is determined in the petroleum laboratory by use of a modified Ostwald pipette, of which the Fenske routine-type viscometer is the most popular. Because of the burden of work imposed by the Diesel fuel study, additional instruments had to be procured and facilities provided for handling more instruments. The work in connection with this and other studies requires viscosity determinations to be made at two or sometimes more temperatures, which has necessitated the installation of a second thermostatically controlled bath to reduce the time required to perform a definite task. Special high-precision viscometers (the Fenske Master Viscometer) were procured in connection with the Aviation Gasoline Survey, and, because of their larger physical dimensions, a special bath and controls were constructed and assembled.

Molecular weight is of considerable importance and interest in connection with the correlation of the physical properties of petroleum fractions. For this reason, two modified, Menzies-Wright, ebullioscopic, molecular-weight apparatuses and accessory equipment have been obtained and installed. This equipment makes possible the determination of molecular weight to be made in 30 minutes.

The 77-plate fractionating column from which much information on the character of distillates from various important American crude oils was obtained during the recent war was completely overhauled when jacket thermocouples, vital to efficient control, failed. This column is in almost continuous use, formerly in analyzing distillates from crude oils but now principally in purifying hydrocarbons required in research work. In addition to this column, two new types of fractionating equipment have been received, an Oldershaw all-glass bubble-plate column and a 12-foot Podbielniak column.

Synthesis and Purification of Hydrocarbons

The synthesis of special hydrocarbons, unavailable in commerce, was continued in 1947, although considerably curtailed by lack of personnel and press of more urgent work. In the preparation of the diphenyl series of compounds the following have been prepared or are in nearly complete state of preparation by synthetic processes:

1. Diphenylmethane
2. 1,2-Diphenylethane
3. 1,3-Diphenylpropane

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4. 1,4-Diphenylbutane
5. 1,5-Diphenylpentane
6. 1,1-Diphenylethane
7. 1,1-Diphenylpropane
8. 1,1-Diphenylbutane
9. 1,1-Diphenylpentane

The relationships of the several diphenyls are shown in figure 22. The identification of these compounds, or even the families of hydrocarbons to which they belong, in petroleum fractions can be accomplished only when their physical properties are known. Their behavior in certain analytical procedures and their role in and effect on combustion characteristics are also facts that need elucidation. The pure compounds are essential for all of these uses. As a class, these dicyclic aromatic compounds are of particular importance because their presence in jet propulsion fuels may increase the tendency of the fuel to form carbon deposits in vital parts of the jet engines and because their presence in Diesel fuels will lower the cetane number of these fuels.

In addition to the diphenyl-type hydrocarbons, members of the naphthalene series appear in the kerosine and higher boiling range petroleum fractions. To obtain similar fundamental data on these hydrocarbons, commercial-grade samples of several of these types have been procured for further purification. Among these are alpha- and beta-methylnaphthalene, three of the ten possible dimethylnaphthalenes and the two hydrogenated naphthalenes, tetralin and decalin. Of these hydrocarbons, tetrahydronaphthalene and 2-methylnaphthalene after treatment are now in a fair state of purity.

Some effort has been made to purify commercial 1-methylnaphthalene, the low primary reference standard used in Diesel fuel testing. All samples of this material so far investigated have been found to be badly contaminated, principally with 2-methylnaphthalene, but nonhydrocarbon materials also were found to be present.

Material has been obtained and work begun on the synthesis of spiropentane. Because of other more pressing work it was necessary to postpone this investigation. This material is of importance to the Thermodynamics Section, where heat capacity and heat of combustion data are needed.

Silica Gel Adsorption

Mention has been made of the use of silica gel for making separations between hydrocarbon types. This method also can be used as an analytical tool, although it offers some difficulties in the Diesel fuel boiling range. For straight-run aviation gasoline base stocks, by far the largest percentage of hydrocarbons present are naphthenes, paraffins, and aromatics. By observing the progress of the filtration, by means of refractive index measurements, a quantitative separation between the naphthenes and paraffins as a group and the aromatics can be made. In higher boiling distillates, such as those in which the Diesel fuel study is concerned, the situation becomes much more complex. In these boiling ranges, dicyclic and condensed ring naphthenes and dicyclic and condensed ring aromatics appear in petroleum distillates together

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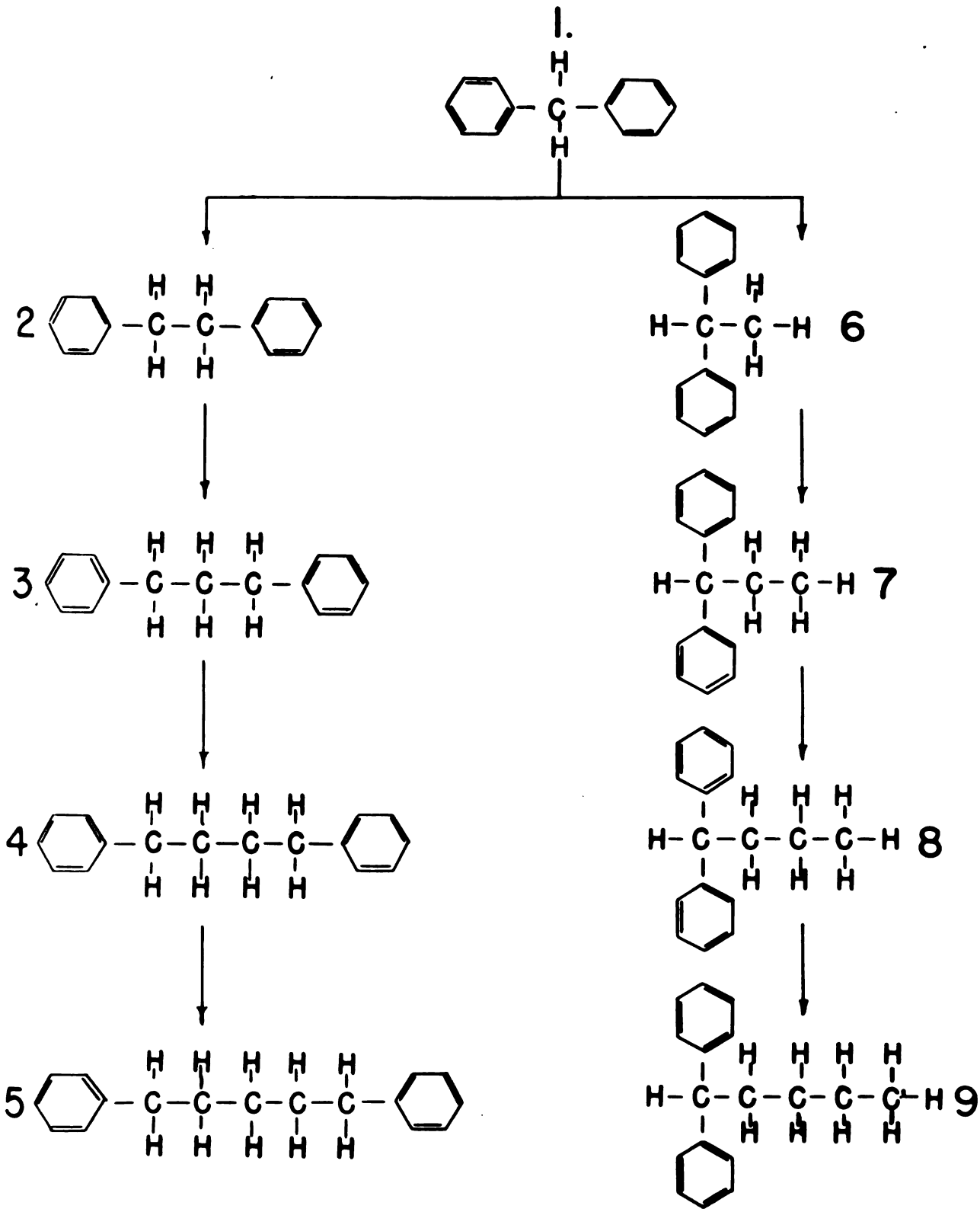

Figure 22. - Chart showing relationships of various diphenyl aromatic hydrocarbons being synthesized.

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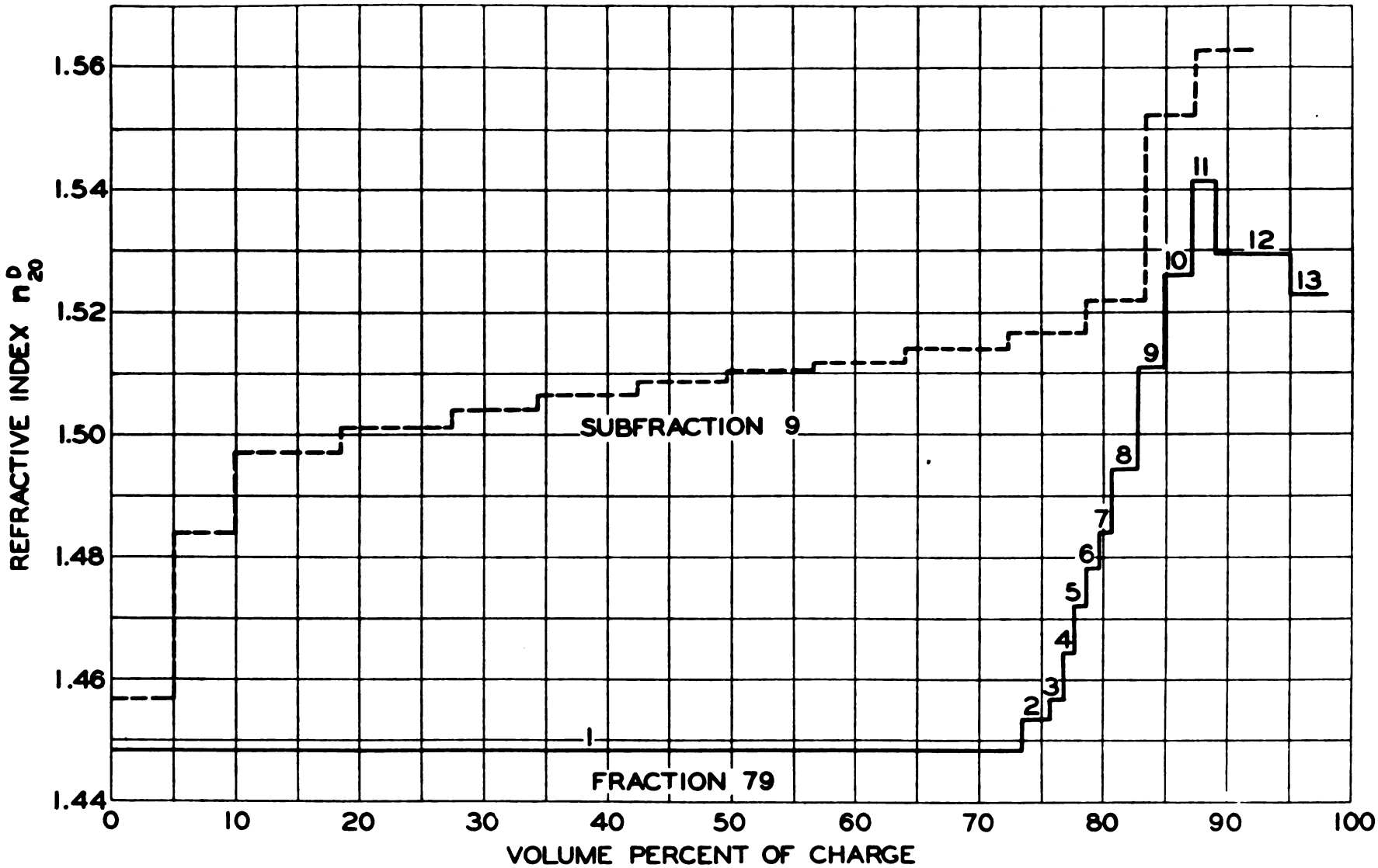

Figure 23. - Typical adsorptograms obtained by filtration of Diesel oils through silica gel.

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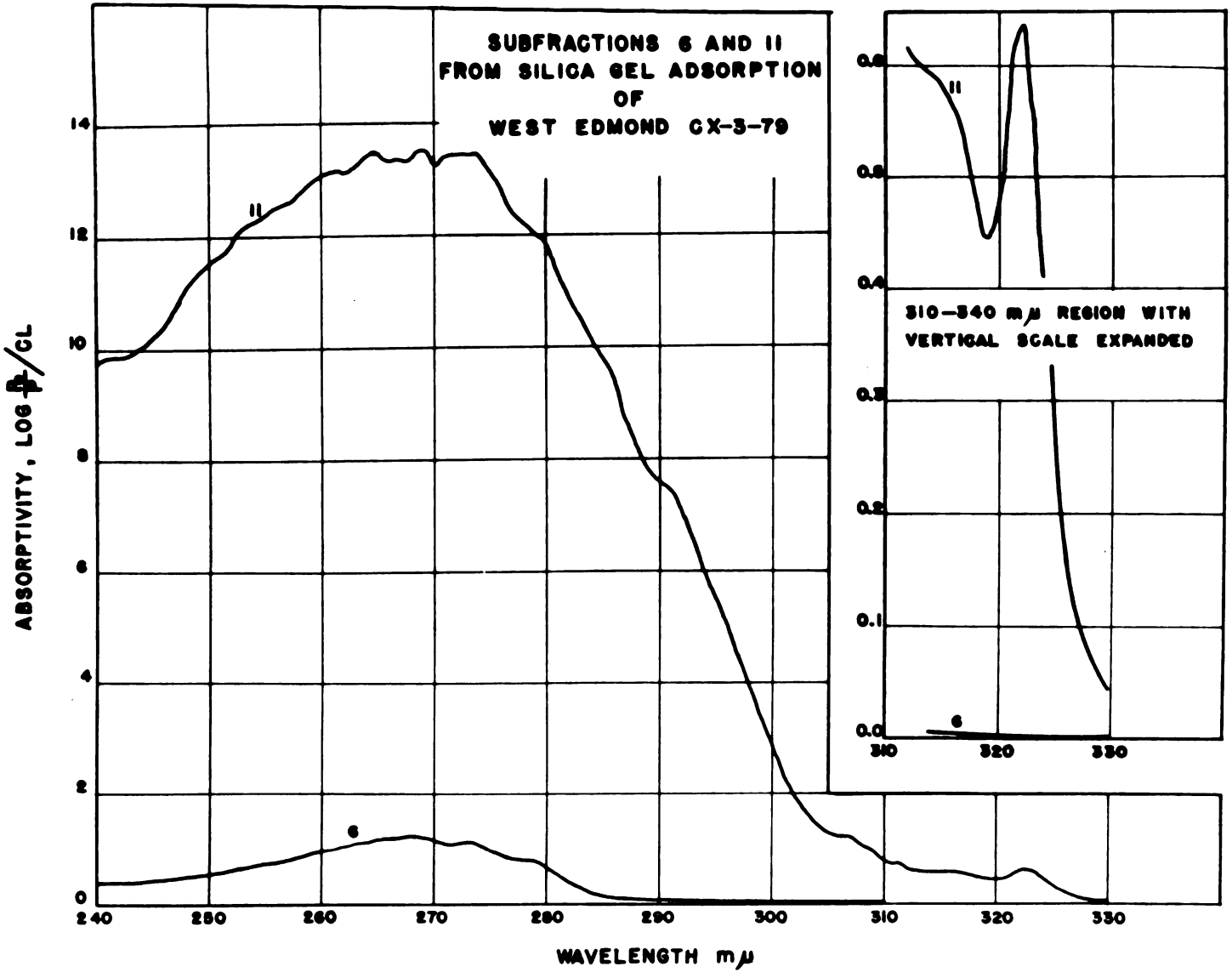

Figure 24. - Ultraviolet absorption curves of Diesel fuel fractions.

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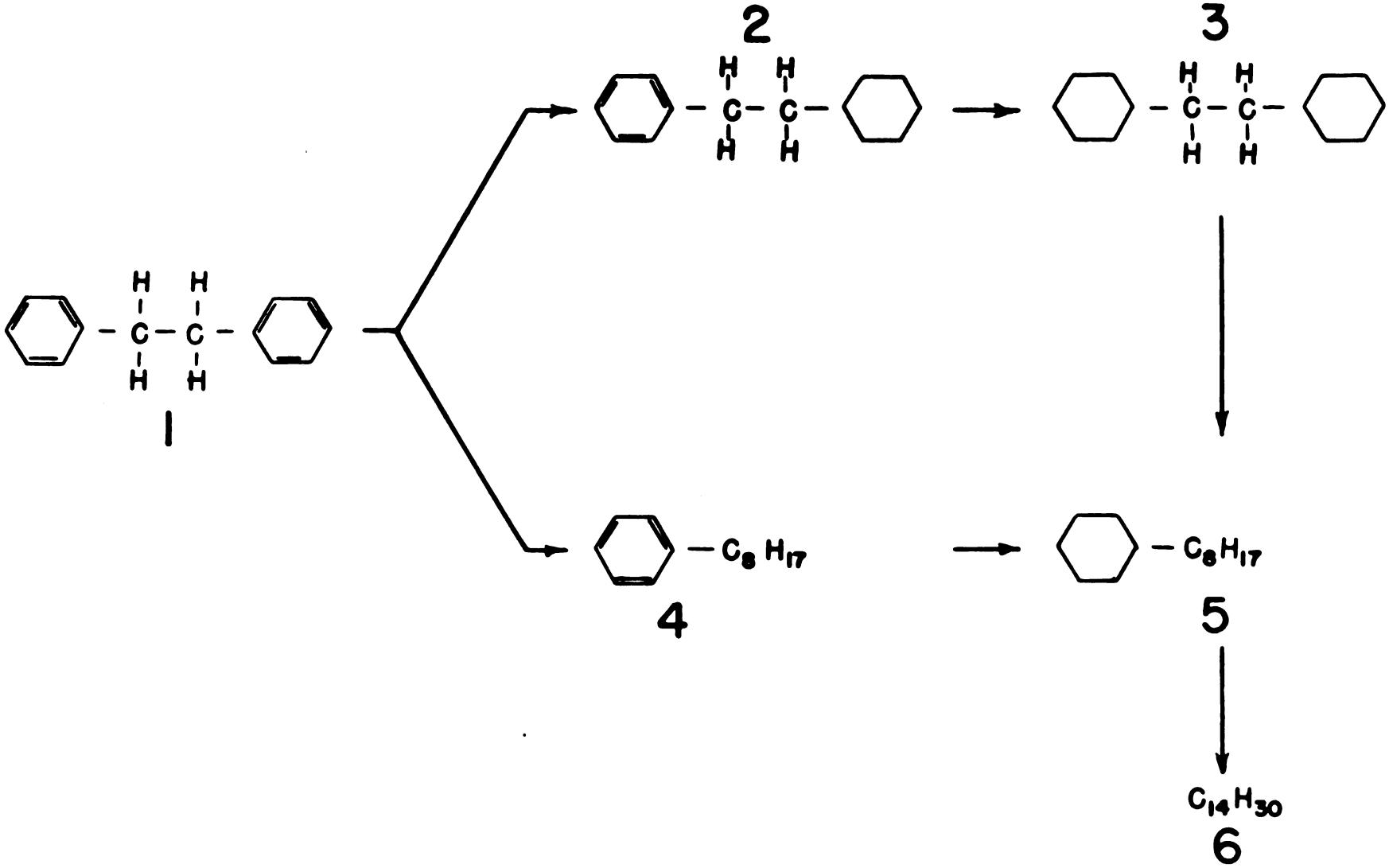

Figure 25. - Compounds used to study change in infrared absorption caused by change in molecular structure.

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with, under some circumstances, sulfur compounds and olefinic hydrocarbons. In the present work, only straight-run distillates are under investigation. Hence, hydrocarbons from cracking reactions (olefinic) are kept at a minimum, and from choice of original crude oil, the sulfur is low in content although probably not absent. Figure 23 shows a typical adsorption separation for a narrow fraction (495°-498° F.) in the Diesel fuel boiling range and for a rerun of subfraction 9 of the original silica gel filtration. By means of fluoresence (supported by ultraviolet analyses at questionable points) the first appearance of aromatics in the percolate can be detected. Thus, the paraffin-naphthene portion can be obtained with an extremely small amount of aromatics. On the contrary, the aromatic portion will contain a considerable quantity of hydrocarbons not aromatic in structure. At present, this is tolerated but not desired. In the silica gel separation it has been suspected recently that dicyclic naphthenes are appearing between paraffins-naphthenes and aromatics, because a refractive index slightly above that of the paraffin-naphthene mixture has been noted. This is and will continue to be the subject of investigation. Above a refractive index of approximately 1.48, hydrocarbons of the naphthalene family should appear. This is substantiated in figure 24, showing ultraviolet absorption curves of subfractions 6 and 11 (fig. 23) where the absorption peaks in the vicinity of wave length 322 millimicrons, characteristic of naphthalenes, are small in the absorption curve of subfraction 6 but significant for subfraction 11.

Infra-red Adsorption Spectrometry

In cooperation with Prof. J. Rud Nielsen of the University of Oklahoma, the infra-red spectra of six high-boiling compounds whose presence in Diesel fuels is suspected have been determined. These hydrocarbons have been selected because of their structural relationships and are:

1. 1,2-diphenylethane
2. 1-phenyl-2-cyclohexylethane
3. 1,2-dicyclohexylethane
4. 1-phenyloctane
5. 1-cyclohexyloctane
6. n-tetradecane

These compounds possess very nearly the same molecular weight, and one phase of this study will be to determine, if possible, the effect of structure upon infra-red adsorption spectra. The different structures involved are shown in figure 25.

The method of determining carbon and hydrogen in distillates by combustion in a lamp was published.41/

Properties of and Analyses for Sulfur Compounds

The increasing utilization of crude oils containing sulfur and the lack of fundamental data concerning the sulfur compounds of petroleum have caused

41/ Simmons, M. C., Determination of Carbon and Hydrogen in Petroleum Distillates: Ind. Eng. Chem., anal. ed., vol. 19, June 1947, pp. 385-389.

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the Bureau of Mines to enter into a fundamental study of sulfur compounds. This study will include the determination of physical properties for the common sulfur compounds, establishment of analytical methods for various types of sulfur compounds, and determination of effects which such sulfur compounds may have upon petroleum products as well, as studies in the removal of sulfur compounds or their conversion to products with less harmful effects.

A survey of the literature to establish the present status of fundamental work on organic sulfur compounds has been completed. The first difficulty encountered in this survey was the question of nomenclature. As a result, a study was made of the various forms of nomenclature in use, and certain recommendations were made to govern nomenclature in future publications on sulfur compounds. These recommendations are given in a report[42/] which is the first of a series entitled "Sulfur in Petroleum."

As a result of the literature survey, the second report[43/] in the series "Sulfur in Petroleum" has been published, giving selected values for the boiling points, freezing points, densities, and refractive indices of sulfur compounds containing less than 14 carbon atoms. In addition, this report gave a resume of work that has been done in the identification of sulfur compounds from petroleum and its products. An additional report is being prepared which lists calculated functions, such as specific dispersion, refractivity intercept, parachor, and molecular volume for the same group of sulfur compounds.

Quantities of pure sulfur compounds are being prepared for more accurate determinations of their physical properties. In particular, they will be useful for determination of patterns for instrumental methods of analysis such as ultraviolet, infra red, and mass spectrometry. Thiophene, 3-thiapentane (ethyl sulfide), and 2-thiabutane (methyl ethyl sulfide) have been prepared in quantities greater than 1-1/2 liters and with a purity higher than 99.9 percent by the freezing-point method. In addition, smaller amounts of lower-purity material have been prepared in the cases of 1-pentanethiol, 3,4-dithiahexane (ethyl disulfide), 1-dodecanethiol, and 4,5-dithiaoctane (propyl disulfide).

Study of Asphalts

As a result of increased interest in the utilization of bitumen or oil from impregnated sands and shales, a study was made of the asphaltic portion of an extract of the Edna bituminous sands of San Luis Obispo County, Calif. This extract was prepared at the San Francisco office by extraction of the sands with a Diesel-oil solvent. Removal of the solvent was followed by a Bureau of Mines distillation analysis of the residuum. The properties of the

42/ Ball, John S., and Haines, William E., Sulfur in Petroleum. Nomenclature of the Sulfur Compounds in Petroleum: Chem. and Eng. News, vol. 24, 1946, pp. 2765-9.

43/ Haines, William E., Wenger, Welton J., Helm, R. Vernon, and Ball, John S., Sulfur in Petroleum. II. Boiling Points, Freezing Points, Densities, and Refractive Indices of Some Sulfur Compounds: Bureau of Mines Report of Investigations 4060, 1946, 42 pp.

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residual bitumen and of two asphalts prepared from this residuum were determined by common asphalt tests. The asphalts from the Edna sands resembled asphalts of the same penetration from Oregon Basin, Wyoming, crude oil and had properties that were intermediate between the properties of asphalts prepared from crude oils from Tampico, Mexico, and Kern River, California, oil fields. Cracking experiments also have been carried out on the recovered bitumen to indicate the suitability of the oil for various uses.

Considerable time was spent assembling for publication the laboratory data obtained on 131 asphalts prepared from (1) 25 crude oils of Wyoming, Montana, Arkansas, California, and Mexico; (2) a native bitumen of Rozel Point, Utah; (3) extracted bitumen of Athabaska tar sand located near Fort McMurray, Alberta, Canada; and (4) extracted bitumen from the Edna bituminous sand in San Luis Obispo County, California. A laboratory method for determining the compositions of asphalts in terms of three groups of constituents known as oils, resins, and asphaltenes, was developed and has been prepared for presentation at the American Chemical Society meeting in New York in September 1947 and for publication in one of the journals of the society.

THERMODYNAMICS OF PETROLEUM

In recent years there has been a marked trend in the petroleum industry toward the use of petroleum as a raw material for the production of pure hydrocarbons. The hydrocarbons are, in turn, utilized in the production of many industrial chemicals. In order to produce these chemicals efficiently, chemists and chemical engineers require thermodynamic data that will aid them in working out processes and in designing the equipment used in the manufacturing processes. For example, thermodynamic data enable us to calculate the theoretical maximum yield from a given chemical reaction, and in addition the conditions for the maximum yield may be determined.

In the past, thermodynamic data usually were lacking, and processes were developed by trial and error, backed by chemical and engineering intuition of the designers. Realizing the need for a systematic approach to the problem of building up tables of thermodynamic data, the Bureau of Mines established a research project in 1943 to measure certain thermodynamic properties.

Work has been going on since the initiation of the project, and during the past year investigations were carried on in four specific fields, as follows:

Low-Temperature Calorimetry

One of the important thermodynamic quantities is entropy. This term does not have very much significance to the layman, but it relates to energy changes involved in all chemical reactions, and the chemist or engineer should know the entropies of the reactions to devise processes and to design equipment.

The entropy of a compound can be calculated from heat-capacity data determined from extremely low temperatures up to the temperature at which the value of the entropy is required. For this reason, systematic measurements

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of heat capacities of hydrocarbons have been carried on in the laboratory at the Petroleum Experiment Station, Bartlesville, Okla., over the temperature range 12° to 300° K. (-433° to +80° F.) and higher.

Organic compounds are characterized by the large number of isomers corresponding to a given elementary composition. By isomers is meant compounds having the same elements and in the same proportion but differing in the manner in which the elements are grouped together. The physical properties of the compounds and the isomers usually differ. Because of this complexity, it has seemed profitable to study certain series of isomers to determine the effect of branching upon the thermodynamic properties. Accordingly, low-temperature measurements were made on the five hexanes. The elementary formula for hexane is C_6H_{14}, but, owing to the different ways of arranging the atoms in the molecule, there are five compounds corresponding to this formula. The results of the studies on these compounds were published in an article in the Journal of the American Chemical Society.44/ Another similar study was made on the pentenes. The elementary formula for these materials is C_5H_{10}, but, owing to peculiarities of the compound, the number of possible isomers is six. The results of this investigation were published in an article in the Journal.45/

An article by H. M. Huffman46/ describes briefly the usefulness of thermodynamic data and methods of application. The article further describes the equipment in use for the production of low temperatures and the calorimetric methods employed. This information is of value to those who wish to evaluate the quality of the Bureau's work.

Vapor-Heat Capacity

Many industrial processes are carried out at high temperature and in the vapor phase, so it becomes of interest to extend the temperature range of measurements discussed in the preceding section. To obtain values of the entropy for the vapor state, the thermodynamic laboratory is making measurements of the heats of vaporization and of the specific heat of the vapors over the temperature range 25° to 200° C. (77° to 392° F.)

Measuring vapor heat capacities with a high degree of accuracy is very difficult, and considerable time and effort have been devoted to developing equipment that yields measurements of high quality. The method and the results of experimental work on two heptanes are described in a publication by Waddington, Todd, and Huffman.47/ The results obtained are highly precise,

44/ Douslin, D. R., and Huffman, H. M., Low-Temperature Thermal Data on the Five Isomeric Hexanes: Jour., Am. Chem. Soc., vol. 68, 1946, p. 1704.

45/ Todd, S. S., Oliver, G. D., and Huffman, H. M., The Heat Capacities, Heats of Fusion, and Entropies of the Six Pentenes: Jour., Am. Chem. Soc., vol. 69, 1947, p. 1519.

46/ Huffman, H. M., Low-Temperature Calorimetry at the Bartlesville Station of the Bureau of Mines: Chem. Rev., vol. 40, 1947, p. 1.

47/ Waddington, G., Todd, S. S., and Huffman, H. M., An Improved Flow Calorimeter. Experimental Vapor Heat Capacities and Heats of Vaporization of n-Heptane and 2,2,3-Trimethylbutane: Jour., Am. Chem. Soc., vol. 69, 1947, p. 22.

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and it is believed that they are also highly accurate. These data will begin to meet a long-standing need, as accurate vapor-heat capacities have been woefully lacking in the past. An interesting byproduct of these measurements has been the obtaining of information as to imperfection of the vapors. This is quite important, as no real gas obeys the ideal gas laws, and an equation of state based on experimental observations of the pressure, volume, and temperature relations is necessary to make calculations for systems involving real gases.

Combustion Calorimetry

In addition to the entropy discussed previously, another important thermodynamic quantity is the enthalpy. For organic compounds, this quantity is most readily obtained from the heat of combustion. Accordingly, studies are being made of heats of combustion. This work has been directed primarily toward working out methods for measuring the heat of combustion of derivatives of hydrocarbons. These derivatives are extremely important industrially because of their many commercial uses.

In the combustion process, the methods are extremely difficult to study, because the main combustion reaction is accompanied by some side reactions. Methods for the combustion of compounds containing sulfur and chlorine have been worked out that yield fair accuracy, and the work is being continued in the hope of improving accuracy.

Statistical Calculations

The use of statistical mechanics to calculate thermodynamic properties from spectroscopic and molecular data is a potentially powerful tool to extend the experimentally measured quantities as well as to calculate the desired quantities without reccurse to thermal measurements. At present this method is restricted to relatively simple molecules because of inability to interpret the spectra.

Studies are being carried out in which the experimentally determined quantities are used to supplement the spectral data; hence, thermodynamic properties are calculated to 1,500° K. and higher with considerable reliability for even complex molecules. These calculations have been made for thiophene, benzene, and 2-methyl-2-butene but have not been published.

A great many of the data obtained in this laboratory have been made available to industry through cooperation with A.P.I. project 44.

NATURAL-GAS RESEARCH

In its work on petroleum and natural gas the Bureau of Mines has enjoyed the cooperation of the American Gas Association for many years on the study of various problems relating to the operation of natural-gas pipelines. New problems have developed as old ones have been completed, and this has resulted in a more or less continuous existence of cooperative work with the Association.

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During the war, all research on pipeline operational problems was discontinued, owing to assignment of the Bureau's engineers to other essential war work. With the cessation of hostilities, one prewar project was reactivated and two new projects were started.

Natural-Gas Hydrates

Natural-gas pipelines have been operated at progressively higher pressures during the past two decades. With the higher pressure, the operators found that plugs of solid, white, and icelike material would form at times in the pipelines when the pipeline temperature was known to be well above the freezing temperature of water. These plugs sometimes would completely stop the flow of gas through the line. The plugs were found to be caused by the formation of compounds known as natural gas hydrates. The Bureau with the cooperation of the American Gas Association began a study of these hydrates in 1935 and the research was actively pursued at the Amarillo Helium Plant until war conditions made it necessary to discontinue the work. The hydrate study was so nearly completed, that in the postwar period it was decided not to reactivate laboratory research but, rather, continue activities to the preparation of a summary report. Such a report has been prepared and is scheduled to be published.[48] This report will complete the scheduled work on the hydrate problem.

During the study of natural-gas hydrates, Bureau engineers developed an apparatus to determine the dew point of gases under pressure. This apparatus now is used widely throughout the natural-gas industry. At the request of the chairman of the American Society for Testing Materials Committee D-3 on Gaseous Fuels, the Bureau has prepared a tentative standard for a dew-point method of determining the water-vapor content of gaseous fuels based on the use of this apparatus.

Flow of Natural Gas in Pipelines

During the past 10 to 15 years, developments in the transmission of natural gas such as the use of large-diameter pipe, high operating pressures, and high velocities have outdistanced technical research on basic flow problems. As a result, present gas pipeline flow formulae are not accurate enough for predicting the carrying capacity of large pipelines or for calculating their operating efficiences. Recognizing this deficiency, the Natural Gas Department of the American Gas Association entered into a cooperative agreement with the Bureau of Mines in September 1946 to conduct a thorough study of the factors influencing flow of gas in pipelines. This was the first new cooperative study with the Association. The investigation was divided into four main phases:

1. Review of literature and present usage.
2. Studies of fundamentals in the laboratory and on comparatively short sections of pipelines.

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[48] Deaton, W. M., and Frost, E. M. Jr., Gas Hydrates and Their Relation to the Operation of Natural Gas Pipe Lines: Bureau of Mines Monograph 8. In press.

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3. Field studies on long pipeline systems.
4. Correlation of data and development of conclusions.

The first phase was substantially completed during the fiscal year, and a report[49] was prepared summarizing review of literature and present usage of pipeline-flow formulae. This paper advanced a tentative method for the solution of pipeline-flow problems based upon published results of American, British, and German research.

Removal of Nitrogen from Natural Gas

Natural gases consist of mixtures of hydrocarbons, carbon dioxide, nitrogen, helium, and other gaseous compounds. Among these constituents, carbon dioxide, nitrogen, and helium are noncombustible and adversely affect the heating value of the natural gas. The percentage of the constituents vary widely in gases from field to field, but fortunately the noncombustible constituents in the natural gases produced in most of the fields of this country are in low enough concentrations so as not to affect seriously the heating values. However, in some important fields of the Nation, the higher nitrogen contents of the natural gases and the corresponding reductions in heating values are the concern of many within the natural-gas industry. In some areas, relatively large reserves of natural gas have been developed that have limited or no marketability because of low heating values. Elsewhere, large pipeline systems are operating at near-capacity loads, with demand for gas increasing. In many instances pipelines are transporting natural gases containing 10 percent or more of nitrogen, which is noncombustible. One suggested solution for both of these situations is the removal of a large portion of the nitrogen from the natural gas. This would accomplish the two-fold purpose of increasing the heating value of the gas and increasing the effective capacity of the pipeline by decreasing the specific gravity and viscosity of the gas - two properties that tend to impede flow.

This subject is of interest in helium production, as helium-bearing natural gases commonly contain 10 to 80 percent nitrogen, which reduces the calorific value and may affect adversely the ready and profitable sale of residue natural gas following helium extraction. Further, the low-temperature process used for helium extraction has excellent prospects for application, with some minor modifications, to permit coincidental extraction of nitrogen as well as helium.

The subject is of interest to the natural-gas industry, also, because it concerns marketability of high-nitrogen-content natural gases, and the efficiency of transmission and net deliverability of pipeline systems transporting gas to markets. Hence, the American Gas Association, representing the

49/ Ferguson, J. W., Pipe-Line Flow Studies. Part I: Review of the Literature and Analysis of the Flow Equation, Presented at the Meeting of the Natural Gas Section of the American Gas Association, Spring Meeting, Chicago, Illinois, April 30-May 1, 1947, and printed by the Association as a part of the "Interim Report by Subcommittee on Pipeline Flow."

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industry, is cooperating with the Bureau of Mines in research on nitrogen removal. This is the second cooperative research project initiated this fiscal year. The Association's cooperation for the year was limited to research involving a survey of literature, patents, and prospective industrial methods of nitrogen removal.

Research studies on means for removal of nitrogen from natural gas were initiated in January 1946 by the Bureau of Mines and were continued throughout fiscal year 1947 at the Amarillo helium plant. Thus, prior to execution of the cooperative agreement with the American Gas Association, a partial review of the literature had been made and studies were in progress on low-temperature processing cycles similar to the helium-extraction cycle. Some experimental work on a pilot-plant scale was initiated on a helium-production unit at the Exell helium plant, but it was interrupted shortly thereafter to devote full time to the literature research.

Preliminary studies indicate that nitrogen removal by low-temperature processing of natural gas, i.e., by liquefaction and fractionation, can be made practical and economical under most conditions where such removal is of interest. However, additional experimental data are needed. Much interest in both the subject of nitrogen removal and the proposed work by the Bureau has been manifested by members of the gas industry.

HELIUM UTILIZATION AND RESEARCH

The late war directed attention very forceably to the importance of research to our country's industrial development and progress. Helium is no exception to this, and the Bureau of Mines is aggressively conducting research, within the limited funds made available to it, toward the appraisal of the Nation's helium resources, improvements in processing cycles and equipment, and in increasing its utilization through the development of new uses and better procedures. This research program is headquartered at the Bureau of Mines Helium Plant, Amarillo, Tex.

Helium Survey

Helium in large quantities is obtained solely from natural gases, and the only way to find new reserves of helium is to analyze natural-gas samples as wildcat wells are drilled into new gas-producing formations and new fields are discovered. Although the present reserves of helium appear to be adequate for abundant utilization, it is self-evident that unless new reserves of helium are found, production will stop as soon as the present reserves are depleted.

Since World War I, the Bureau of Mines has conducted a survey to determine the helium resources of the Nation. During fiscal year 1947, 500 helium analyses and 229 combustion analyses of natural-gas samples were made in search for new reserves of helium-bearing natural gas.

When a natural gas having a helium content high enough to permit efficient extraction is found, Bureau engineers study the available geological and engineering information on the field to determine whether enough gas is present to warrant consideration of the field as a helium reserve.

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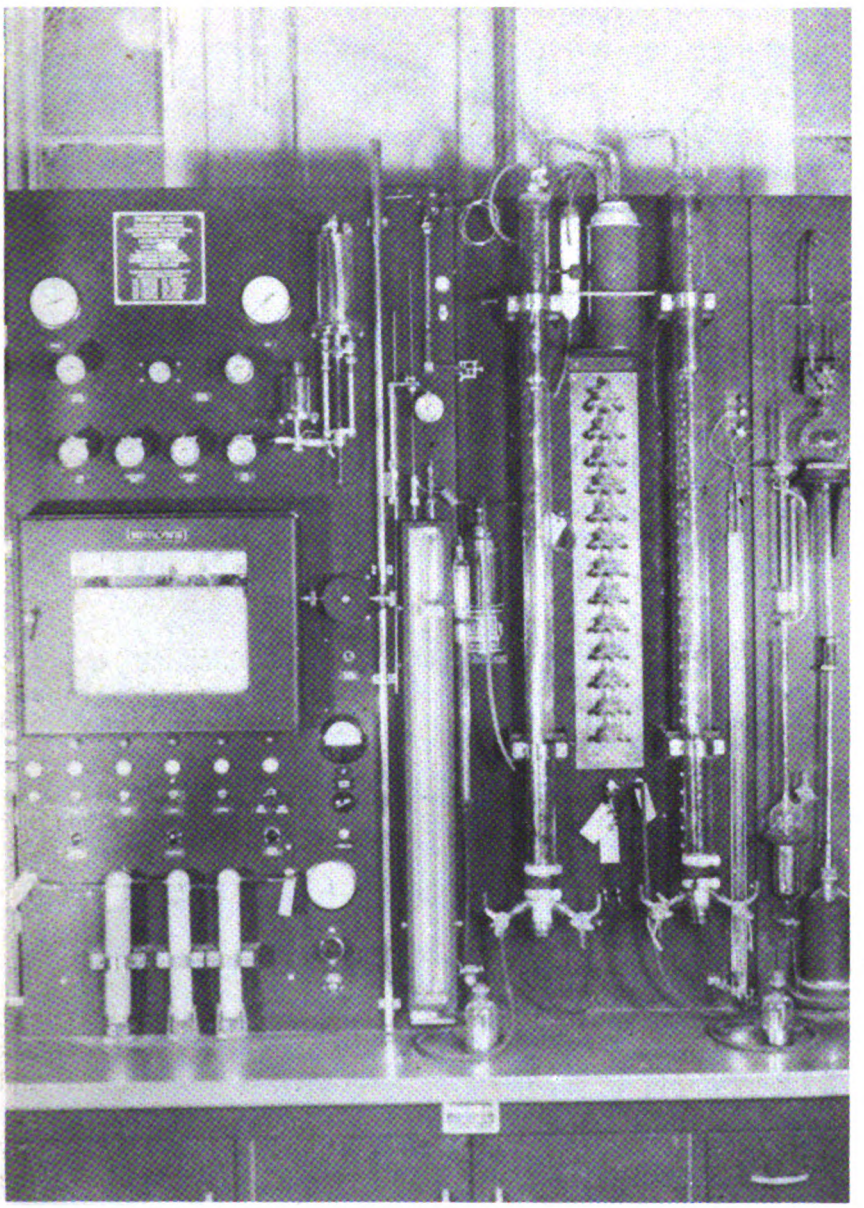

Figure 26. - Automatic, low-temperature, gas-fractionating columns.

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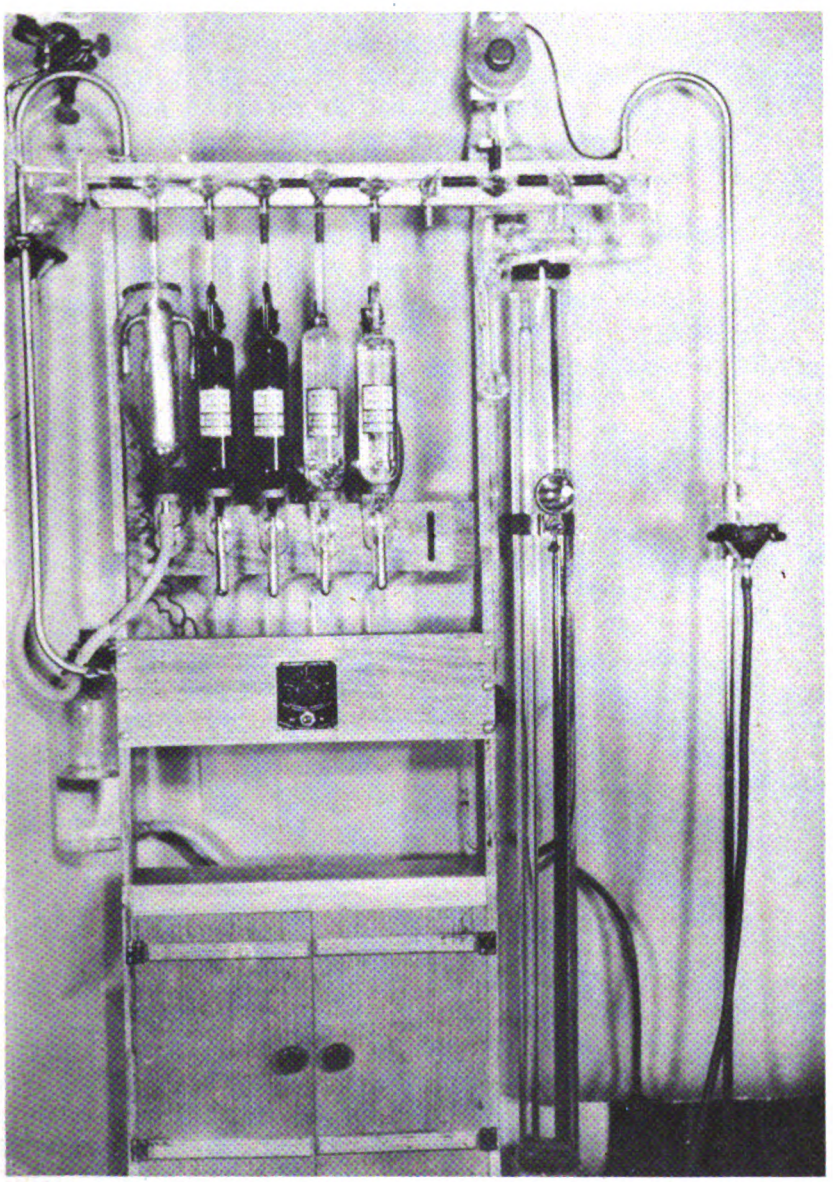

Figure 27. - Orsat gas-analysis equipment.

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A deep-test well was drilled in the Rattlesnake field on the Navajo Indian Reservation in San Juan County, northwestern New Mexico, in 1942, and an analysis made in the Bureau laboratory revealed that the gas from it contained about 7.6 percent helium. This was an unusually high helium content, and as the result of studies of the field, the Government opened negotiations with the Navajo Indian Tribe and the leaseholders to acquire all of the high helium-content natural gas as a Government helium reserve. These negotiations were completed and were ratified by Congress during this fiscal year, thus giving the Government an additional helium reserve where the helium can be held in place until it is needed. An engineering report on the field was published.50/

An interesting use of the Bureau's improved helium-analysis apparatus51/ was developed this year to discover casing leaks in wells. Over 230 helium analyses and 65 Orsat analyses were made on samples from a field where gas was suspected of leaking into some of the oil wells from a high-pressure upper sand. Comparison of the helium content of gas from the upper sand with gas being produced with the oil from the wells indicated the affected areas in this particular field. Additional tests to locate casing leaks in individual wells are being planned. The successful completion of this research will give the industry a useful tool.

The helium survey laboratory is well-equipped to handle a wide variety of gas analyses. The equipment consists in part of automatic low-temperature fractionating columns (fig. 26), combustion analysis equipment (fig. 27), sulfur-determination equipment, compressibility equipment, special hydrogen and oxygen analysis equipment for detecting minute volumes of each, equipment for determining the specific gravity of gas, and a recording calorimeter for determining the heating value of gas. This equipment, together with a mass spectrometer, a charcoal fractionator, and a viscosimeter, provides the laboratory with equipment for the complete chemical and physical analysis of natural gas.

Process Development Research

Large-scale production of 100-percent helium is the ultimate goal of research on improving purity. Already there is a demand for pure helium. The Bureau of Mines plants normally produce helium of 98.2 to 98.5 percent purity, nitrogen with a very small amount of hydrogen being the impurities. To meet the demand, experimental work on a pilot plant was started in fiscal year 1946, utilizing activated charcoal at temperatures in the range of -50° F. to -300° F. to remove the remaining impurities. The trial operations were successful in producing a helium of 99.8 plus percent purity, the impurity being principally hydrogen. Small quantities of this high-purity helium have

50/ Hinson, H. H., Reservoir Characteristics of Rattlesnake Oil and Gas Field, San Juan County, New Mexico: Bull., Am. Assoc. Petrol. Geol., vol. 31, No. 4, April 1947, pp. 731-771.

51/ Frost, E. M., Jr., Improved Apparatus and Procedure for the Determination of Helium in Natural Gas: Bureau of Mines Report of Investigations 3899, June 1946, 16 pp.

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been produced for experimental use. Consideration has been given to removal of hydrogen to produce an even purer product.

The results of this research showed clearly that almost pure helium could be produced by the addition of the activated charcoal step to the regular plant extraction process, and a decision was made to install charcoal-adsorber vessels or purifiers on all helium purification units at the Exell plant. Scarcity of materials caused a long delay in the delivery of stock required for pressure-vessel fabrication; however, these were received and were being machined and fabricated at the close of the fiscal year.

The separation of helium from natural gases is accomplished by subjecting the source gas to very low temperatures (in the order of -300° F.) while the gas is under pressure. During World War II the Bureau of Mines found an abundant supply of helium-bearing natural gas under a reservoir pressure in excess of 3,000 psi. in the Rattlesnake field, New Mexico.52/ The process developed previously for separating helium from natural gas operated at a maximum pressure of about 600 pounds per square inch, and to process the new gas in one of these units it would be necessary to reduce the pressure from 3,000 to 600 pounds. This represented the loss of a tremendous amount of energy that could not be recovered in a practical manner, while at the same time it was necessary to put energy into other parts of the separation system. It therefore seemed appropriate that special consideration be given to the design of a process specially suited to the gas and utilizing to best advantage the high pressure under which the gas is available.

Work has progressed on the compilation of basic factors regarding the gas to be processed, the rates of flow, the pressures and temperatures in various parts of the process cycle, and similar data needed in designing a process and the equipment for extracting helium from Rattlesnake gas. Some study has been given to various process designs to utilize the available high pressure in Joule-Thomson cooling, but considerably more study will be required. Heat-exchange equipment needed in the low temperature cooling cycle has been given considerable thought. A tentative design of an extended surface heat exchanger suitable for a high-pressure helium-separation unit has been devised. A model of the design is shown in figure 28. Construction of an experimental heat exchanger of this design and tests on its capacity and efficiency are planned for the forthcoming fiscal year.

USES OF HELIUM

Helium in Welding

One of the recently developed uses of helium is in helium shielded-arc welding. In this welding process, helium is used to prevent air from coming in contact with the molten metal and the hot solidified metal in the immediate vicinity of the weld.

52/ See footnote 50.

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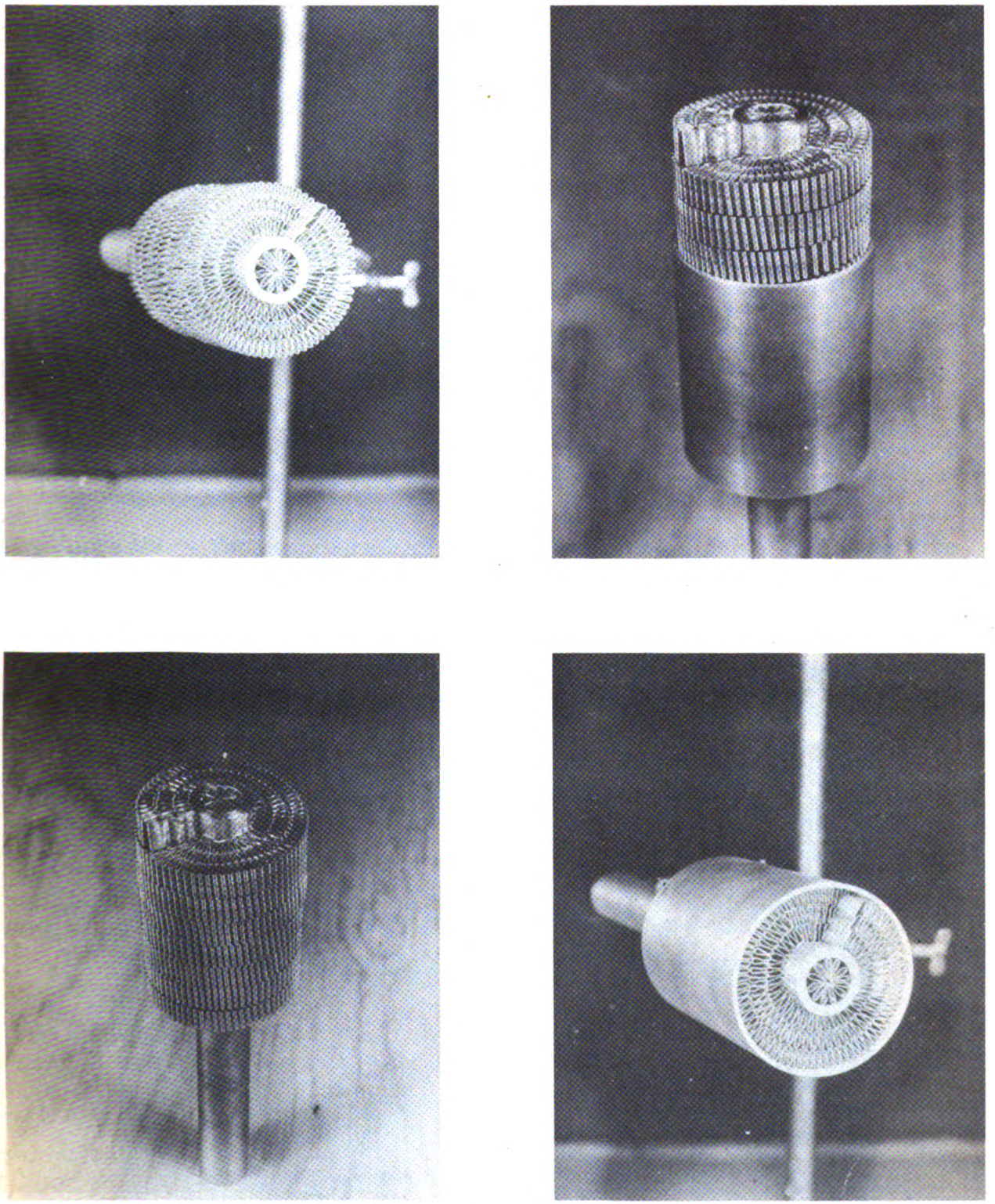

Figure 28. - Newly designed extended surface heat exchanger.

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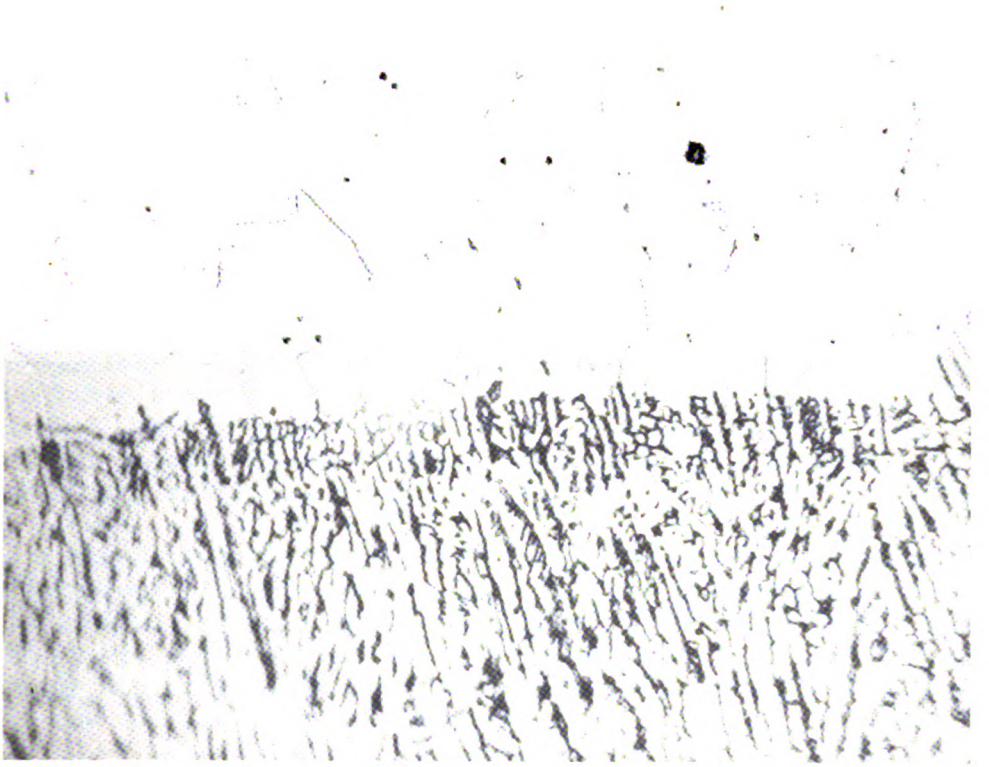

Figure 29. - Photomicrograph of weld on stainless steel. Weld made with helium shielded-arc process.

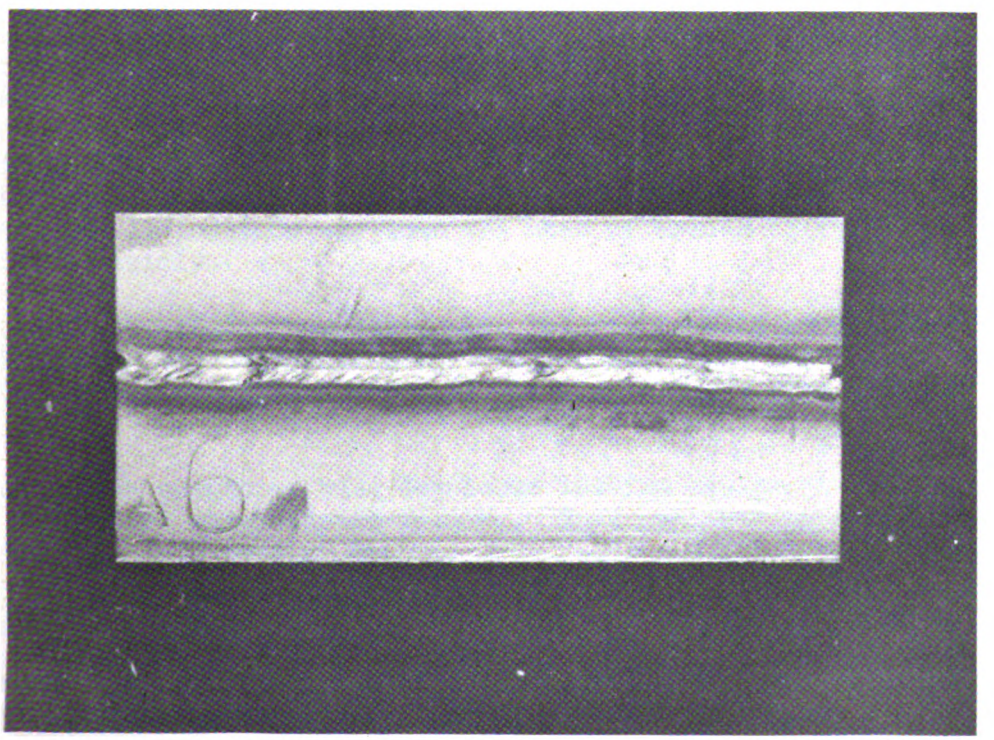

Figure 30. - Butt weld on 1/16-inch titanium sheet welded with helium shielded-arc process.

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The Bureau of Mines, anticipating the importance of this new application of helium, initiated a welding research program to collect and make available to industry and the public information and data that will be useful in numerous welding applications. Initial work on the program was done in the General Electric Co.'s welding research laboratories in Schenectady, N. Y. Helium of various degrees of purity was tried in the preliminary experiments, and the result indicates that high-purity helium apparently produced better welds - at least on aluminum. Initial tests have not been conclusive, but the Bureau of Mines has taken steps to produce commercial helium of 99.8 percent purity. The initial work was completed at the General Electric laboratories, and a welding-research laboratory was established at the Amarillo Helium Plant for continuation of the shielded-arc welding studies.

The advantages of this type of welding now have been realized, and the process is being applied to welding metals such as aluminum, stainless steel (fig. 29), magnesium, copper, and inconel. One of its most recent applications has been the experimental welding of titanium (fig. 30). As of this date, the shielded-arc is the only means known for welding this metal which offers much promise as a new material for construction.

Experiments dealing with several phases of helium shielded-arc welding have been started. Research has dealt primarily with thin-gage material less than 1/8 inch thick. Each new welding study involves numerous variables, and many of the variables in helium shielded-arc welding are critical. Some of these involve current density, voltage, arc speeds, gas flow, electrode size, height of electrode above the work, and proper shielding of the weld metal as it cools. Proper shielding of the weld metal to prevent oxidation is of utmost importance if good welds are to be obtained, and considerable time has been spent in studying gas flow and proper shielding of the molten metal.

Soundness of the welds has been determined by bend tests, tensile tests, and metallographic examinations. Results of experiments made so far are very encouraging, and indications are that the uses of helium shielded-arc welding are developing rapidly.

Samples of shielded-arc welding made in the Amarillo welding laboratory were on display at the Salt Lake City, Utah, Centennial Exposition. Reports received from the Exposition state that the samples created a great deal of interest.

Several large companies have developed welding equipment that is now available for helium shielded-arc welding. This application of helium promises to be one of the large postwar uses.

Helium in Metallurgy

A program has been initiated to study the possibilities of using helium for extinguishing magnesium fires. During a heat treatment of magnesium castings, furnace temperatures often exceed predetermined values, with the result that the magnesium ignites and causes serious fires. In this investigation, magnesium castings will be heated to the ignition point, and experiments will

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be made to determine the possibilities of using helium-controlled atmospheres for extinguishing the fire.

A Bausch & Lomb microscope and metallurgical equipment for grinding and polishing specimens have been mounted in the metallurgical laboratory. This equipment was purchased for the preparation and microscopic examinations of metals. Metallographic examinations have been made on sections from numerous weld samples to study the soundness of the welds and the effect of helium shielded-arc welding on various metals.

Helium as a Tracer Gas

Work on the development of the use of helium as a tracer gas in oil and gas fields was carried on throughout the fiscal year. When used as a tracer gas, helium is mixed in relatively small volumes with the natural gas that is being injected into an underground reservoir. Variations in the helium content of gases produced from various parts of the reservoir when helium has been added as a tracer to the injected gas give valuable and long-sought data on the direction and rate of travel of the injected gases.

The arrival of the tracer-laden gas at producing wells is detected by analyzing the produced gas. The detection is facilitated by drawing graphs showing the helium content of the produced gas on various days. Several typical graphs of the helium content of gas from producing wells after helium has been added as a tracer in the injected gas are shown in figure 31. In addition to revealing the arrival of injected gas at a producing well, these helium content data will permit calculation of the volume of injected gas that is mixed with the natural gas being produced.

Reports have been published53/54/ covering some of the Bureau's helium tracer-gas work. During the present fiscal year, a cooperative helium tracer-gas project with the Pure Oil Co. was started in the Cabin Creek, W. Va., field. Information was desired on the comparative value of different programs for adding helium to the injected gas, and the work was planned accordingly. In a previous project,55/ helium was added in concentrations of 0.14 percent by volume for approximately 2 weeks and 0.05 percent for approximately 30 days. In the Cabin Creek study, tracer helium was added in three different concentrations, 1 percent by volume for 7 days, 5 percent for 4 days, and a slug of essentially pure helium.

The collection of data at this project is not yet complete, but for each concentration the use of the helium tracer gas permitted following the wave of injected gas as it moved through the producing formation and provided information that otherwise could not have been obtained as conveniently by any other

53/ Frost, E. M., Jr., Helium Tracer Gas Studies in the Elk Hills, Calif., Field: Bureau of Mines Report of Investigations 3899, June 1946, 6 pp.

54/ Frost, E. M., Jr., Improved Apparatus and Procedure for Determining the Helium Content of Natural Gas: Bureau of Mines Report of Investigations 3897, June 1946, 6 pp.

55/ See footnote 53.

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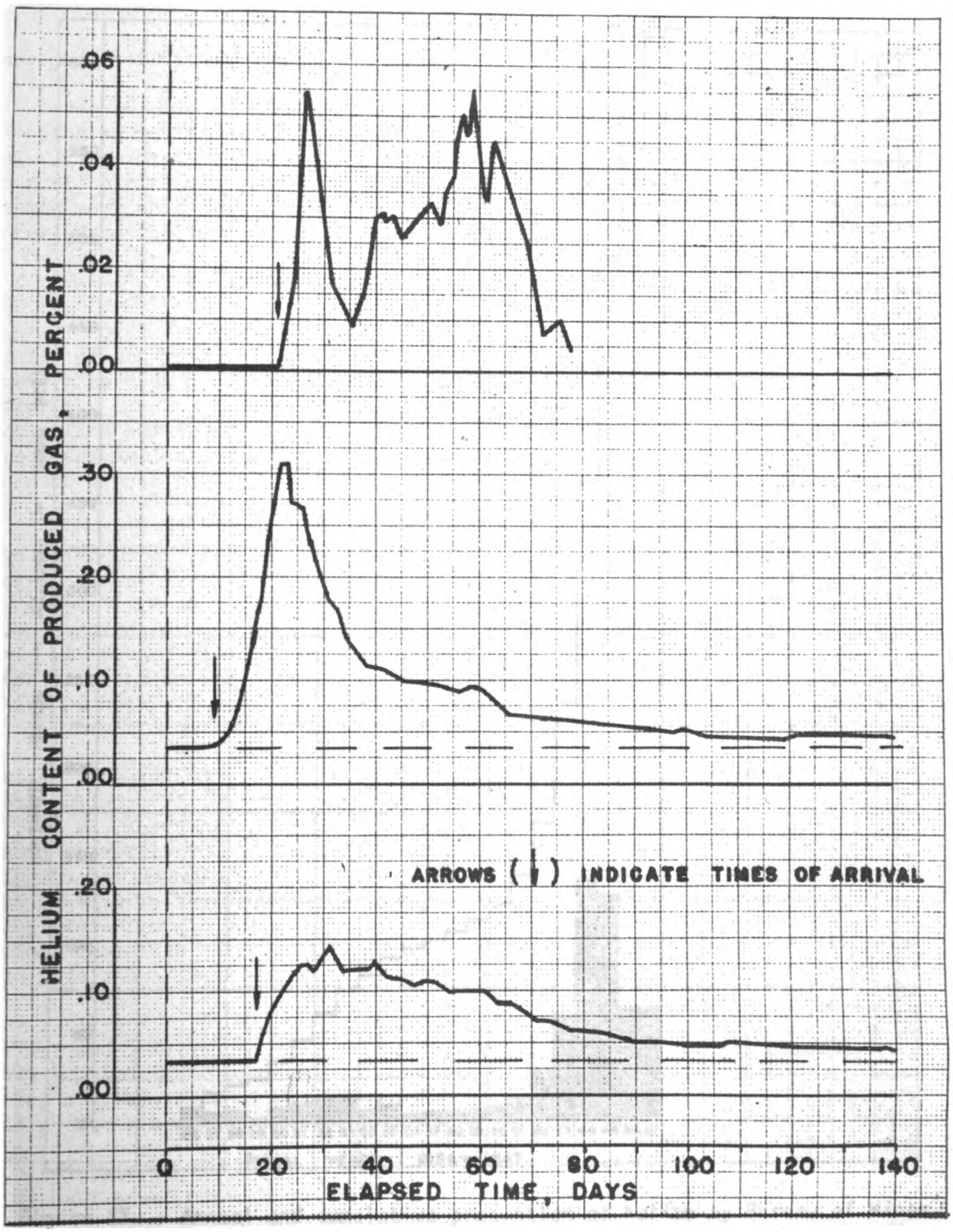

Figure 31. - Typical graphs showing arrival of tracer-laden injected gas at producing wells.

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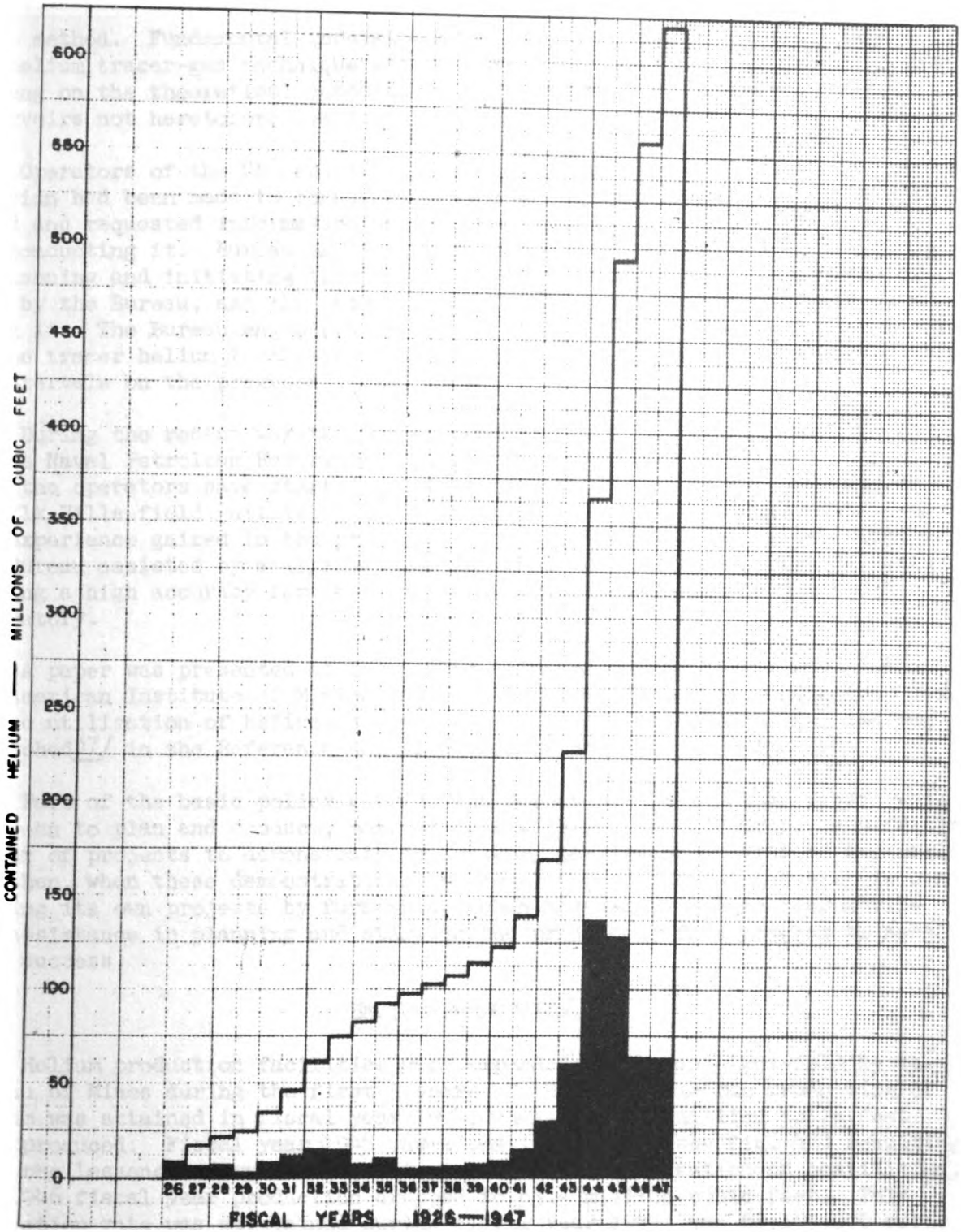

Figure 32. - Annual and cumulative production of helium by Bureau of Mines helium plants.

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known method. Fundamental information on the more efficient application of the helium tracer-gas technique was obtained, and the study is providing data bearing on the theoretical concepts of flow of gases through underground reservoirs not heretofore available.

Operators of the Shuler, Ark., field, advised the Bureau of Mines that a decision had been made to conduct a helium tracer-gas project in the Shuler field and requested information and assistance from the Bureau in planning and conducting it. Bureau engineers consulted with the Operating Committee in planning and initiating the project. Analytical apparatus was made available by the Bureau, and the technicians of the operators were trained in using it. The Bureau engineers organized the project, supervised the addition of the tracer helium to the injected gas, and have consulted with the operators at intervals on the progress of the work.

During the recent war the Bureau conducted a helium tracer-gas project in the Naval Petroleum Reserve No. 1, Elk Hills, Calif., field.56/ Since then the operators have started a helium-tracer project in another part of the Elk Hills field, utilizing their own personnel and resources along with the experience gained in the previous tracer study conducted by the Bureau. The Bureau assisted by analyzing some duplicate gas samples to aid in establishing a high accuracy for the analytical results produced in the field laboratory.

A paper was presented at the fall meeting of the Petroleum Division of the American Institute of Mining and Metallurgical Engineers, Galveston, Tex., on the utilization of helium as a tracer gas in oil and gas fields, and was published57/ in the Reference Annual number of the Petroleum Engineer.

Part of the basic policy guiding the Bureau of Mines helium-tracer work has been to plan and conduct, more or less with its own resources, a sufficient number of projects to demonstrate to industry the practicability of the process and then, when these demonstrations are completed, to assist industry in conducting its own projects by furnishing, when necessary, engineering advice and assistance in planning and starting the projects. This program is meeting with success.

HELIUM PRODUCTION

Helium production facilities were expanded more than eight-fold by the Bureau of Mines during the first 3 years of the war. Maximum production of helium was attained in fiscal year 1944, when over 137 million cubic feet were produced. Fiscal year 1945 saw a small decrease (see fig. 32) resulting from the lessened enemy submarine menace. With the cessation of hostilities, the 1946 fiscal year production dropped to 63.4 million cubic feet. This production rate was maintained during fiscal year 1947, and 63,199,000 cubic feet were produced.

56/ See footnote 53.

57/ Frost, E. M., Jr., Use of Helium as a Tracer in Oil and Gas Fields: Petrol. Eng., vol. 18, No. 10, 1947, pp. 140, 142, 146, 148, 150, 152.

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This helium was produced at the Amarillo and Exell Helium Plants. The Amarillo Helium Plant processes helium-bearing natural gas from the Cliffside field, Potter County, Tex., a Government-owned reserve of some 50,000 acres. By curtailing production at the Amarillo plant it is possible to conserve the Cliffside reserve for future emergencies. This was done in 1947, and only about one-eighth of the annual production was extracted at the Amarillo plant. The remainder was produced at the Exell Helium Plant, which is situated on a pipeline that transports helium-bearing natural gas from the Panhandle gas field to commercial markets whether or not the helium is extracted. If the helium is not extracted prior to use of the gas as a fuel, it is lost forever. Thus, operation of the Exell plant makes an abundant supply of helium available to Governmental, commercial, and medical users and at the same time preserves the Government-owned reserves for future needs.

Conservation of helium that otherwise would go to market with the natural gas, if not extracted by the Exell Helium Plant, was continued during the year by storing it underground in the Cliffside gas field. About 7.2 million cubic feet of helium, which was produced by the Exell plant in excess of current demand, were delivered to underground storage during this fiscal year. As this conservation program was instituted in 1945, the Bureau of Mines has stored 56.7 million cubic feet of helium in underground storage. This helium is returned to the Cliffside field through a 2-inch high-pressure pipeline that connects the Amarillo and Exell plants and the Cliffside gas field. The pipeline, which is of unique construction, was described in a trade journal.58/

In addition to the two helium plants that were operated in fiscal year 1947, the Bureau of Mines has two plants that are maintained in standby condition. These are the Otis helium plant at Otis, Kans., and the Navajo helium plant at Shiprock, N. Mex. They were built during the war and are kept in condition to be operated when needed. The Otis plant, when operating, also processes helium-bearing natural gas, which flows to commercial markets, and the helium content is being lost while the plant is in standby status. The Navajo plant, when operating, processes gas from the Government-owned reserve in the Rattlesnake field which, like the Cliffside gas field, is being held and preserved for National emergencies and future needs. A fifth helium plant, the Cunningham, ceased operations between V. E. and V. J. Days. This plant was an important producer of helium during the war, but because of dwindling helium-bearing natural gas reserves to supply the plant, the decision was made to dismantle it. Special helium-extraction equipment was removed and stored for future use. Other equipment and materials were transferred to projects of the Bureau of Mines. Things that could not be used efficiently by the Bureau and the Department were declared surplus property to the War Assets Administration. This agency assumed custody of the remaining surplus property on December 1, 1946, and the Cunningham helium plant passed into history.

As a part of the program of placing the Rattlesnake field in a standby status, closing tools were installed in the bottoms of the tubing, first above

58/ Reynolds, Jack J., High-Pressure Pipe Lines Transport Valuable Helium at 2800 psi.: Oil and Gas Jour., vol. 45, No. 23, Oct. 12, 1946, p. 34.

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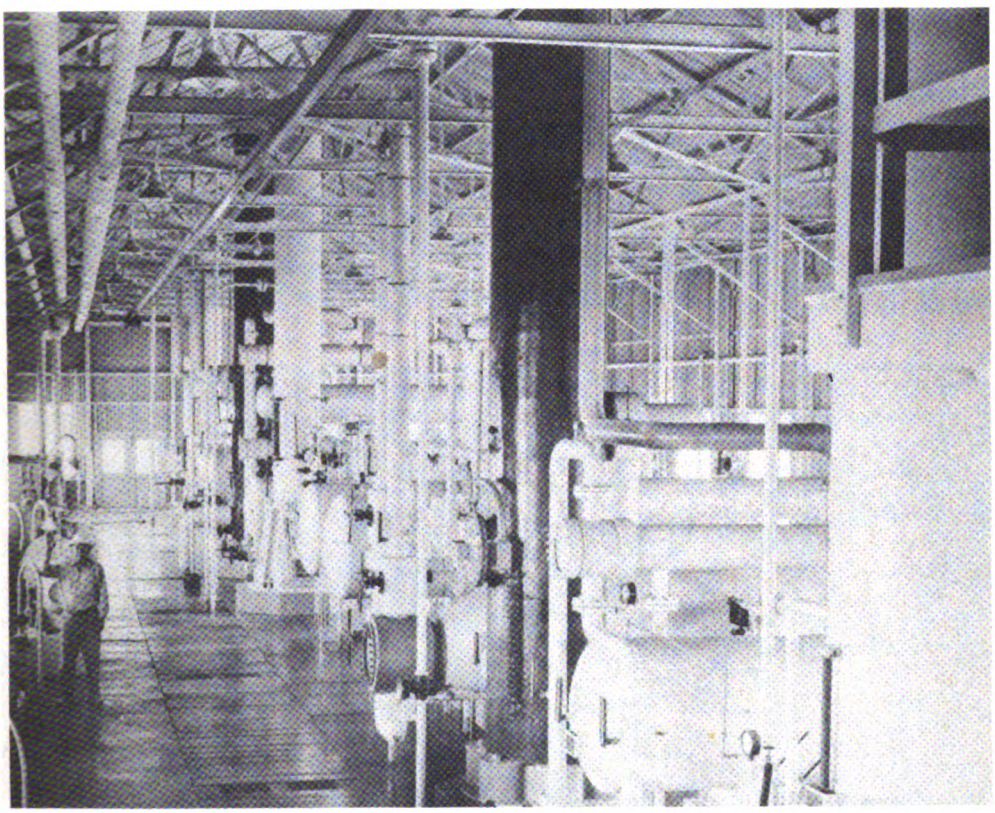

Figure 33. - Interior of gas-penetrating building, Navajo plant.

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Figure 34. - First-aid and safety meeting at Bureau of Mines Exell helium plant.

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the packers, in the two high-pressure helium-bearing gas wells. These closing tools prevent any flow of gas from the wells, even though the casing heads and Christmas trees may be damaged. The closing tools can be removed in a few hours with wire line equipment, and the wells would be ready to produce gas.

Corrosion-protective equipment (magnesium anodes) was installed along the 90 miles of high-pressure, 2-inch, helium pipeline connecting the Navajo helium plant with the railway shipping terminal at Gallup, N. M. The installation is not complete, but tests show that some protection already is afforded the entire line, and approximately 90 percent of it is protected better than the minimum recognized by corrosion engineers as being enough for complete protection from corrosion.

The Bureau of Mines supplies helium to the Navy, Army, Weather Bureau, Public Health Service, and other Governmental agencies for use in blimps, meteorological balloons, medical treatment, diving, caisson operations, scientific research and other activities. Pursuant to the amended Helium Act (50 Stat. 885, 50 U.S.C. 161-166), the Bureau of Mines sells helium to non-Federal users. This helium is employed in many ways, including medical use and such commercial applications as helium shielded-arc welding and metallurgical processes. In fiscal year 1947, Governmental agencies took 69 percent of the production while the sales to non-Federal users amounted to 21 percent, which was a threefold increase in commercial sales over any previous year.

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